CANADIAN
JOURNAL OF RESEARCH

CONTENTS

Notice to Contributors

THE RESONANCE METHOD FOR MEASURING THE RATIO OF THE SPECIFIC HEATS OF A GAS, C_p/C_v

PART II[1]

BY A. L. CLARK AND L. KATZ

Results

Nitrogen

The gas used was obtained from the Ohio Chemical and Mfg. Co., who gave its purity as 99.8%, with air making up the major portion of the remaining 0.2%. Because of this high purity the gas was used as supplied.

TABLE II

COLLECTED VALUES OF MEASUREMENTS, CORRECTIONS, AND RESULTS FOR NITROGEN—23.0° C.

Press., atm.	Frequency at resonance	Λ	G	χ	$\Delta\gamma$	$\gamma_{exp.}$	$\gamma_{corr.}$
0.9984	27.38_9	1.00084	1.00021	1.00011	0.0148	1.387_2	1.402_4
3.668	52.70_1	1.00307	1.00072	1.00002	0.0056	1.401_5	1.408
5.389	63.95_9	1.00452	1.00102	1.00002	0.0042	1.406_5	1.412_5
6.751	71.64_4	1.00566	1.00123	1.00002	0.0036	1.410_5	1.416
8.056	78.27_8	1.00675	1.00142	1.00002	0.0032	1.412_5	1.417_5
10.516	89.54_7	1.00881	1.00172	1.00001	0.0027	1.419	1.424
13.032	99.81_8	1.01092	1.00195	1.00001	0.0023	1.426	1.431
15.659	109.39_7	1.01313	1.00214	1.00001	0.0021	1.428_5	1.433_5
21.219	127.64_3	1.01777	1.00227	1.00001	0.0017	1.441_5	1.446_5
25.929	141.39_9	1.02171	1.00213	1.00001	0.0015	1.453_5	1.458*

* *Using Verschoyle's (20) Pv data instead of P.T.R. this value of $\gamma_{corr.}$ was found to be 1.459.*

The values of γ and the various correction factors applied are listed in Table II. The Λ and G factors were calculated from the Pv equation*

$$(Pv)_{23.0°} = 1.08470 - 0.2354 \times 10^{-3}P + 2.8230 \times 10^{-6}P^2, \qquad (50)$$

which was found by interpolation† of the P.T.R. (Holborn and Otto) data on nitrogen as given in Handbuch der Experimentalphysik (9). It was found that the final corrected values of γ could be represented, to within experimental error, by a straight line. The equation of this straight line,

[1] *Part I appeared in the February issue.*

* *To change v in Amagat units to cubic centimetres per gram, the factor 799.42 given by Deming and Shupe was used.*

† *Whenever a sufficient number of values were available, interpolation in this paper was carried out by means of the Gauss interpolation formula.*

fitted to the data by the method of least squares, was found to be

$$\gamma = 1.4003 + 2.21 \times 10^{-3}P. \tag{51}$$

The values of γ obtained from this equation are, in Table III, compared to those found experimentally.

TABLE III

COMPARISON OF CORRECTED VALUES OF γ FOR NITROGEN WITH VALUES CALCULATED FROM EQUATION (51)

Press., atm.	$\gamma_{corr.}$	$\gamma_{calc.}$	$(\gamma_{corr.} - \gamma_{calc.}) \times 10^3$
0.9984	1.402$_4$	1.4025	−0.1
3.668	1.408	1.4084	0
5.389	1.412$_5$	1.4122	0
6.751	1.416	1.4152	+1
8.056	1.417$_5$	1.4181	−1
10.516	1.424	1.4236	0
13.032	1.431	1.4291	+2
15.659	1.433$_5$	1.4349	−1
21.219	1.446$_5$	1.4470	0
25.929	1.458	1.4577	0

The experimental and corrected values of γ are plotted as functions of pressure in Fig. 5 and are compared to those found by Hubbard and Hodge (10), and one value at 20 atm. calculated from the work of Deming and Shupe (4). The straight line through the corrected values was drawn by means of Equation (51). The results are in good agreement at low pressure, but deviate as the pressure increases. Hubbard and Hodge claim an accuracy of 0.2% at atmospheric pressure and 0.4% at the higher pressures. The differences between their values and those of the authors are 0.42% at 10 atm. and 0.76% at 20 atm.
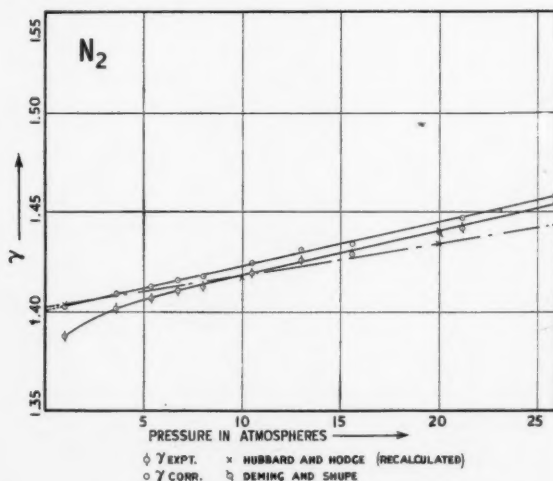

FIG. 5.   Values of γ for nitrogen at 23.0° C.

As the Hubbard-Hodge results were published in the form of a small-scale graph, the authors recalculated the values at 1, 10, and 20 atm. in order to obtain the exact values at these points, using the velocity of sound measurements of Hodge (8) and the same Pv data used by Hubbard and Hodge, i.e., those of Holborn and Otto (9).   The calculations were carried out by means of the Pv equation

$$(Pv)_{27} = 1.09935 - 0.1991 \times 10^{-3}P + 2.737 \times 10^{-6}P^2,$$

obtained by interpolation, and the equation

$$\gamma = W^2\left(\frac{A - CP^2}{(Pv)^2}\right), \tag{52}$$

where W is the velocity of sound, and A and C are the virial coefficients in the above Pv equation.   The values of γ thus obtained fit the Hubbard-Hodge graph very well indeed.   The Deming and Shupe value at 20 atm. (1.44_0) was calculated from their published values of C_v and $C_p - C_v$ and is only slightly lower than that of the authors (0.32%).

The accuracy of the values of γ given in this paper will be considered later. However, a good indication of this accuracy may be obtained by noticing the close agreement between the value of γ at zero pressure as given by Equation (51) and that predicted theoretically for an ideal diatomic gas. As will be seen from the following tables, results may also be reproduced with very great accuracy.

The following values of γ were found for nitrogen on the dates given.

July 15, 1938:	1.401_6
	1.401_4
	1.401_3
Feb. 24, 1939:	1.401_3
	1.400_8
	1.401_0
March 7, 1939:	1.401_2
	1.400_9
Average	1.401_2

At this point the Fortin type barometers were replaced by the home-made barometer already mentioned, and the new values obtained were as follows:

May 9, 1939:	1.402_8
May 23, 1939:	1.401_9
	1.402_6
Average	1.402_4

The averages of the two sets differ by less than 0.09%, with the dispersion about the mean value in each set much less.

Carbon Dioxide

The carbon dioxide was 99.9% pure.   This was determined by absorbing a known volume of the gas in a 33% solution of potassium hydroxide and

measuring the residual volume. To remove any moisture present the gas
was passed through a glass tube surrounded by dry ice. Distilling the gas
over by freezing with liquid air, evacuating over the solid carbon dioxide,
and finally subliming the solid, made no apparent difference in its purity
when tested as described above.

Carbon dioxide is so far removed from the ideal gas state that the correction
factor G is very large and therefore important; it varies strongly with both
temperature and pressure. The only available accurate Pv data are those of
Michels (13, 14) and co-workers who published power series representing their
experimental results at the temperatures: 0°, 25.053°, 29.900° C., etc. They
have pointed out that the virial coefficients for powers higher than the first
are not smooth functions of the temperature, and it is therefore not permissible
to interpolate for intermediate temperatures. As it was desired to obtain
the value of G at 23.8° C., the following method of calculation was adopted:
$G_{25.053°}$ was calculated at the desired pressures from the published Pv equation
at that temperature. Next $\left(\dfrac{\Delta G}{\Delta T}\right)$ was calculated at each pressure from the
25.053° and 29.900° Pv equations, and finally $G_{25.053°}$ was corrected to $G_{23.8°}$
as follows:

$$G_{23.8°} = G_{25.05°} - \left(\frac{\Delta G}{\Delta T}\right)(25.05 - 23.8). \tag{53}$$

In no case was this correction on $G_{25.05°}$ greater than 0.27% for the range of
pressures involved. Since the Pv data are of great accuracy, it is felt that
the values of G calculated directly from these data are also of great accuracy.
In the calculation of Λ the factor 505.86 was used to change Amagat units
of specific volume to cubic centimetres per gram.

The values of γ found experimentally at the various pressures, corre-
sponding frequencies of resonance, and the correction factors involved are
listed in Table IV. It was found possible to represent the variation of γ
with pressure to within experimental accuracy by a second degree equation.
This was found to be, by the method of least squares,

$$\gamma = 1.2948 + 0.00500P + 0.000179P^2. \tag{54}$$

Values calculated by means of this equation are compared to those found
experimentally in Table V.

The experimental values of γ and the final corrected values are plotted
in Fig. 6 as a function of the pressure. They are compared to a few re-calcul-
ated values from the work of Hubbard and Hodge and two by Worthing.
The graph through $\gamma_{corr.}$ was plotted by means of Equation (54). The
values given by Hubbard and Hodge for this gas were deduced from the
ultrasonic measurements of Hodge and the Pv data of Amagat. To cover
the low pressure range more completely and to obtain more accurate results,
these values were recalculated using the velocity of sound measurements by
Hodge and the Pv data of Michels. While, as pointed out before, the virial
coefficients in Michels' equations are not smooth functions of the temperature,
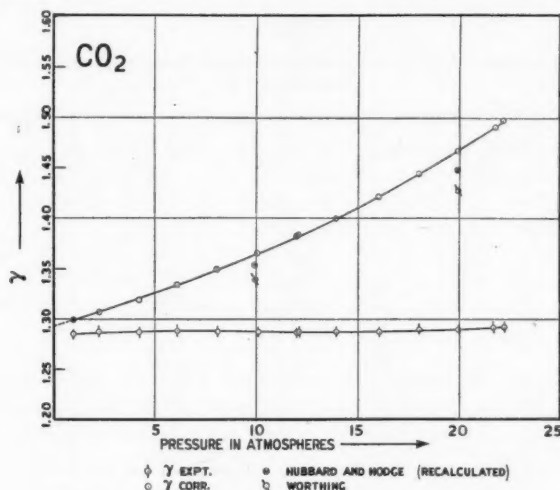
CO_2

FIG. 6.   *Values of γ for carbon dioxide at 23.8° C.*

TABLE IV

COLLECTED VALUES OF MEASUREMENTS, CORRECTIONS, AND RESULTS FOR CARBON DIOXIDE—
23.8° C.

Press., atm.	Frequency at resonance	Λ	G	χ	$\Delta\gamma$	$\gamma_{exp.}$	$\gamma_{corr.}$
0.9917	26.27_0	1.00130	1.00515	1.00002	0.0074	1.285_6	1.299_6
2.273	39.77_0	1.00301	1.01194	1.00002	0.0040	1.288	1.307_5
4.240	54.23_2	1.00567	1.02286	1.00001	0.0026	1.287	1.319
6.119	65.09_0	1.00826	1.03382	1.00000	0.0020	1.288	1.333_5
8.130	74.92_3	1.01110	1.04617	1.00000	0.0017	1.288	1.349
10.103	83.36_8	1.01394	1.05896	1.00000	0.0015	1.287	1.364
12.054	90.91_3	1.01683	1.07234	1.00000	0.0014	1.286_5	1.380_5
12.101	91.12_4	1.01683	1.07270	1.00000	0.0014	1.287	1.382
13.991	97.82_8	1.01976	1.08642	1.00000	0.0013	1.287	1.399_5
16.121	104.83_5	1.02307	1.10286	1.00000	0.0012	1.286_5	1.420
18.071	110.92_0	1.02619	1.11895	1.00000	0.0011	1.289	1.443_5
20.036	116.60_4	1.02941	1.13657	1.00000	0.0011	1.288_5	1.466
21.840	121.64_1	1.03245	1.15317	1.00000	0.0011	1.290_5	1.489
22.223	122.72_8	1.03311	1.15688	1.00000	0.0011	1.292	1.495_5

it was found possible to set up an equation giving values of Pv at 27° C. over the pressure range 0 to 30 atm. to within the desired accuracy. This was possible since coefficients for powers higher than $1/v^2$ could be neglected and the temperature interval of interpolation was very small (between 25.05° and 29.90° to 27°). This equation was found to be

$$(Pv)_{27°} = 1.10635 - 6.0571 \times 10^{-3}\frac{1}{v} + 11.21 \times 10^{-6}\frac{1}{v^2} \tag{55}$$

If we write

$$Pv = A + \frac{B}{v} + \frac{C}{v^2}$$

TABLE V

COMPARISON OF VALUES OF γ FOR CARBON DIOXIDE WITH VALUES CALCULATED FROM
EQUATION (54)

Press., atm.	$\gamma_{corr.}$	$\gamma_{calc.}$	$(\gamma_{corr} - \gamma_{calc.}) \times 10^3$
0.9917	1.299$_6$	1.3000	−0.4
2.273	1.307$_5$	1.3071	0
4.240	1.319	1.3192	0
6.119	1.333$_5$	1.3321	+1
8.130	1.349	1.3472	+2
10.103	1.364	1.3636	0
12.054	1.380$_6$	1.3811	−1
12.101	1.382	1.3816	0
13.991	1.399$_5$	1.3998	0
16.121	1.420	1.4219	−2
18.071	1.443$_5$	1.4436	0
20.036	1.466	1.4668	−1
21.840	1.489	1.4893	0
22.223	1.495$_5$	1.4943	+1

then

$$\gamma = -\frac{W^2}{v^2}\left(\frac{\partial v}{\partial P}\right)_T = \frac{W^2}{2Pv - A + \dfrac{C}{v^2}}. \tag{56}$$

The values of γ obtained from this equation and the measurements of Hodge are at 27°C.; for comparison with those of the authors, they were reduced to 23.8°C. in the following manner.* If it is assumed that Worthing's results on carbon dioxide, though not very accurate in absolute value, are correct relatively to each other for temperature variation, then from his results

$$(\gamma_{27°} - \gamma_{23.8°})_{10 \text{ atm.}} = 1.335 - 1.338 = -0.003$$
$$(\gamma_{27°} - \gamma_{23.8°})_{20 \text{ atm.}} = 1.419 - 1.426 = -0.007.$$

Table VI summarizes these results and compares them to values calculated by means of Equation (54).

The average of seven preliminary tests on carbon dioxide at atmospheric pressure, made during March 1938, compares favourably with the average of three tests made in 1939.

March 10 to 30, 1938: Average of seven tests—1.299$_3$ at 23.1° C.
July 16, 1939:   Average of three tests—1.299$_6$ at 23.8° C.

* The following method was later adopted in calculating γ from the velocity of sound:
By combining Equation (48) and the well known relation between γ and the velocity of sound, the following equation is obtained:

$$\gamma = -\frac{W^2}{v^2}\left(\frac{\partial v}{\partial P}\right)_T = \frac{W^2}{Pv + \dfrac{B}{v} + 2\dfrac{C}{v^2}} = \frac{W^2}{S}.$$

It was found that at constant pressure the values of S calculated from Michels' isothermals are nearly linear functions of the temperature, so that S could be obtained at 27° by direct interpolation between the values at 25.05° and 29.9°.

TABEL VI

COMPARISON OF VALUES OF γ FOR CARBON DIOXIDE GIVEN BY HUBBARD AND HODGE AND AUTHORS

Press., atm.	H. and H. (recalculated) 27° C.	H. and H. 23.8° C.	Clark and Katz 23.8° C.	Diff., %
1	1.300	1.301	1.300	0.07
10	1.349	1.352	1.363	0.81
20	1.439	1.446	1.466	1.36

Hydrogen

The hydrogen was obtained from the same source as the nitrogen. The gas was manufactured by the electrolytic process and was 99.9% pure, with oxygen and a trace of moisture making up the impurity.

The Λ and G factors were calculated from the Pv data of Nijhoff and Keesom (15) interpolated to 24.4° C. (temperature of the gas during the experiment). The Pv equation at this temperature was found to be

$$(Pv)_{24.4°} = 1.088688 + \frac{0.692}{v} \times 10^{-3} \tag{57}$$

G was calculated by means of Equation (26). In the calculation of G, Amagat units of specific volume were converted to cubic centimetres per gram by multiplying by the factor 11127.4.

The values of γ obtained at the different pressures, with the corresponding frequencies of resonance and the various correction factors involved, are summarized in Table VII.

TABLE VII

COLLECTED VALUES OF MEASUREMENTS, CORRECTIONS, AND RESULTS FOR HYDROGEN

Press., atm.	Frequency	Λ	G	χ	$\Delta\gamma$	$\gamma_{exp.}$	$\gamma_{corr.}$
0.9874	26.992	1.00006	0.99943	1.00094	0.0394	1.361_1	1.401_1
2.283	41.389	1.00014	0.99867	1.00030	0.0210	1.38_5	1.404_5
4.161	56.053	1.00025	0.99759	1.00014	0.0133	1.393_5	1.403_5
6.994	72.902	1.00042	0.99597	1.00006	0.0090	1.402_5	1.406
10.088	87.718	1.00060	0.99421	1.00003	0.0069	1.408	1.406_5
12.988	99.680	1.00077	0.99259	1.00003	0.0056	1.412	1.407_5
15.964	110.719	1.00095	0.99093	1.00003	0.0049	1.418	1.410
19.034	121.055	1.00113	0.98924	1.00002	0.0043	1.422	1.411
22.165	130.679	1.00131	0.98754	1.00002	0.0038	1.423	1.409_5
24.961	138.850	1.00147	0.98603	1.00002	0.0035	1.427	1.410_5

Because of the large non-adiabatic compression correction for this gas at low frequencies, the value of γ at atmospheric pressure is rather small. As the pressure increases, the frequency of resonance increases and the value of $\Delta\gamma$ decreases very rapidly (see Table VII), so that at higher pressures the

values of γ may be considered reliable.   If the value of $\gamma_{corr.}$ for atmospheric pressure is neglected, the other values may be represented to within experimental error by a straight line.*   The equation of this line as calculated by the method of least squares was found to be

$$\gamma = 1.4034 + 0.320 \times 10^{-3}P . \tag{58}$$

TABLE VIII

COMPARISON OF VALUES OF γ WITH VALUES CALCULATED FROM EQUATION (58)

Press., atm.	$\gamma_{corr.}$	$\gamma_{calc.}$	$(\gamma_{corr.} - \gamma_{calc.}) \times 10^3$
0.9874	1.401₁	1.4037	(−2.6)
2.283	1.404₅	1.4041	0
4.161	1.403₅	1.4047	−1
6.994	1.406	1.4056	0
10.088	1.406₆	1.4066	0
12.988	1.407₅	1.4076	0
15.964	1.410	1.4085	+1
19.034	1.411	1.4095	+1
22.165	1.409₅	1.4105	−1
24.961	1.410₅	1.4114	−1

Values of γ calculated by means of this equation are compared in Table VIII to those found experimentally.   The values of γ given in Table VII are plotted as functions of the pressure in Fig. 7 with the curve through $\gamma_{corr.}$ drawn according to Equation (58).   The two values by Deming and Shupe (5) were calculated from their published work on hydrogen.   These values agree with those of the authors to within 0.1%.
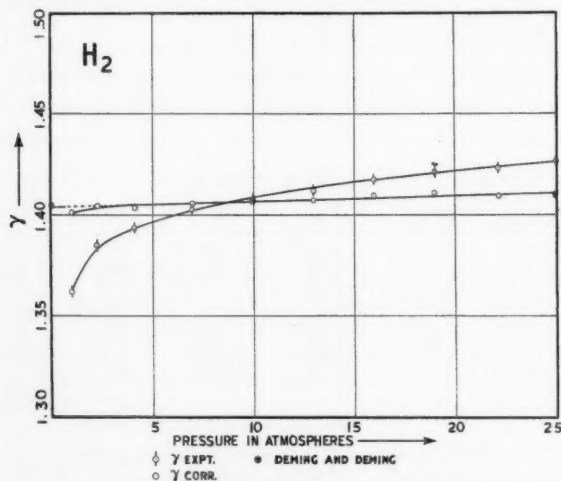
FIG. 7.   *Values of γ for hydrogen at 24.4° C.*

* *See Appendix IV.*

The mean value of seven measurements made in 1938 at atmospheric pressure agree favourably with the mean of three measurements made in 1939.

April 1 to 12, 1938: Mean of seven values—1.400_8 at $24.4°$ C.
August 9, 1939:   Mean of three values—1.401_1 at $24.4°$ C.

The authors consider the values of γ given by Equation (58) more accurate than the individual values found experimentally, as this equation represents the weighted mean of all the measured values.

Argon

Argon of 99.6% purity was obtained from the Ohio Chemical and Mfg. Company.   The 0.4% impurity was mainly nitrogen with a trace of oxygen.

The average temperature of the gas during the test was $24.2°$ C.   Interpolating the Holborn and Otto Pv data as found in the Handbuch der Experimentalphysik to this temperature gave

$$(Pv)_{24.2} = 1.08965 - 0.7146 \times 10^{-3}P + 1.9682 \times 10^{-6}P^2. \quad (59)$$

χ and G were calculated as before from their data.   The factor 560.59 was used to change Amagat units of specific volume to cubic centimetres per gram. The experimental results, together with the various correction factors as applied and the final values of $\gamma_{corr.}$, are listed in Table IX.

TABLE IX

COLLECTED MEASUREMENTS, CORRECTIONS, AND RESULTS FOR ARGON

Press., atm.	Frequency	Λ	G	χ	$\Delta\gamma$	$\gamma_{exp.}$	$\gamma_{corr.}$
0.9886	29.617	1.00117	1.00065	1.00021	0.0252	1.638_8	1.665_8
2.256	44.957	1.00268	1.00146	1.00005	0.0136	1.657	1.673
4.783	65.615	1.00569	1.00307	1.00002	0.0079	1.670	1.683
6.722	77.850	1.00800	1.00426	1.00002	0.0062	1.676_4	1.690
8.741	88.825	1.01042	1.00549	1.00001	0.0051	1.682_8	1.697
10.719	98.440	1.01279	1.00665	1.00000	0.0044	1.689	1.705
12.698	107.166	1.01517	1.00781	1.00000	0.0039	1.694	1.711
14.704	115.354	1.01759	1.00894	1.00000	0.0036	1.699	1.717_8
16.670	122.877	1.01996	1.01003	1.00000	0.0033	1.704_8	1.724_8
18.658	130.060	1.02237	1.01110	1.00000	0.0030	1.710	1.732
20.688	137.038	1.02483	1.01218	1.00000	0.0028	1.716	1.740

As in the case of hydrogen, $\Delta\gamma$ is numerically large at low pressure (low frequency), so that even a small percentage error will greatly affect the final value of γ.   Since the theoretical deduction of $\Delta\gamma$ is for a spherical instead of a cylindrical cavity, one would expect that its values as calculated are on the small side with a corresponding effect on γ.   This was found to be the case.   However, as will be seen from Table IX, $\Delta\gamma$ decreases rapidly with increasing pressure, so that at the higher pressures the same percentage error has a relatively smaller effect on γ.   If the first two values of $\gamma_{corr.}$ are neglected, the other values may be represented to within experimental accuracy by a straight line.   The equation of this line as calculated by the method of least squares was found to be

$$\gamma = 1.6662 + 3.53 \times 10^{-3}P. \quad (60)$$

This equation gives $\gamma_{P=0} = 1.666_2$, which is in good agreement with the theoretical value for an ideal monatomic gas. It is to be noticed that the value of γ at 1 atm. (atmospheric pressure) as given by this equation is 1.670. The authors believe this value to be more accurate than the generally accepted value of 1.667 or 1.668. Values of $\gamma_{corr.}$ are compared in Table X to those calculated by means of this equation, and are plotted in Fig. 8 as a function of the pressure.

TABLE X

COMPARISON OF VALUES OF γ WITH THOSE CALCULATED FROM EQUATION (60)

Press., atm.	$\gamma_{corr.}$	$\gamma_{calc.}$	$(\gamma_{corr.} - \gamma_{calc.}) \times 10^4$
0.9886	1.665$_5$	1.6697	(−4)
2.256	1.673	1.6742	(−1)
4.783	1.683	1.6831	0
6.722	1.690	1.6899	0
8.741	1.697	1.6971	0
10.719	1.705	1.7040	+1
12.698	1.711	1.7110	0
14.704	1.717$_5$	1.7181	0
16.670	1.724$_5$	1.7250	0
18.658	1.732	1.7321	0
20.688	1.740	1.7392	+1

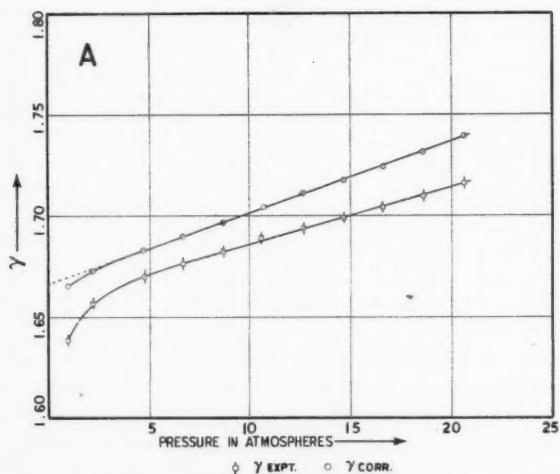FIG. 8. Values of γ for argon at 24.2° C.

Helium

The helium gas was kindly supplied by Prof. J. O. Wilhelm of the University of Toronto. It was of high purity, being evaporated directly from the liquid into an evacuated steel container.

Table XI summarizes the experimental data on this gas and gives the final corrected values of γ. In the calculation of the various correction factors, use

was made of the Pv data of Keesom and Van Santen, which gave by interpolation

$$(Pv)_{23°} = 1.083641 + 0.5400 \times 10^{-3}\frac{1}{v}. \qquad (61)$$

Amagat units were changed to cubic centimetres per gram by multiplying by 5603.33.

TABLE XI

COLLECTED VALUES OF MEASUREMENTS, CORRECTIONS, AND RESULTS FOR HELIUM—23.1° C.

Press., atm.	Freq. at res.	Λ	G	χ	$\Delta\gamma$	$\gamma_{exp.}$	$\gamma_{corr.}$
0.9951	29.11_0	1.00012	0.99955	1.00174	0.0745	1.571_2	1.647_7
2.275	44.59_7	1.00027	0.99897	1.00047	0.0398	1.613_5	1.652_6
5.283	68.54_8	1.00063	0.99760	1.00017	0.0210	1.641_5	1.659
7.871	83.87_4	1.00094	0.99644	1.00010	0.0156	1.650_5	1.660
9.861	94.02_5	1.00118	0.99554	1.00007	0.0131	1.656	1.662
11.754	102.76_0	1.00140	0.99468	1.00006	0.0115	1.659	1.662_5
13.800	111.43_4	1.00164	0.99376	1.00004	0.0102	1.662_5	1.662_5
15.929	119.75_5	1.00190	0.99281	1.00004	0.0091	1.664	1.661_5
17.623	126.04_1	1.00230	0.99205	1.00004	0.0084	1.666_5	1.661_5
19.943	134.10_4	1.00230	0.99101	1.00003	0.0078	1.667_5	1.660

The physical properties of helium are such that, of all the gases, it has the largest correction factor for non-adiabatic compressions. Because of this large correction factor, the values of γ at the lower pressure are not very accurate for reasons already given. Above 10 atm. this correction becomes relatively small (1% or less), being of the same order of magnitude as for nitrogen at atmospheric pressure, and the values may be considered reliable. This is substantiated by the following:

(a) All the values above 10 atm. lie on a straight line whose equation, fitted by the method of least squares, is

$$\gamma = 1.6656 - 2.545 \times 10^{-4}P, \qquad (62)$$

from which the value of γ at zero pressure is found to be, by extrapolation, $\gamma_{P=0} = 1.665_6$, agreeing to within 0.06% of the theoretical value for an ideal monatomic gas*.

(b) The slope of the line passing through the values of γ for higher pressures is almost exactly parallel to a line through some values calculated by Jacyna (11). This is all the more significant when it is borne in mind that though Jacyna's results may not be accurate in absolute value, they are very accurate relatively to one another, so that the slope of the line through them is very accurate.

(c) γ decreases with increasing pressure, a property not found in any of the other gases investigated, but in agreement with predictions from the ex-

* It is to be emphasized that the line was not fitted to the data with the view of obtaining this zero pressure value, but that comparison with one of the other gases, say nitrogen, whose values are all reliable even at the lowest pressure, showed the maximum allowable value of $\Delta\gamma$. In the case of helium, $\Delta\gamma$ falls below this maximum value only above 10 atm. For this reason, only the values above 10 atm. were used; the above results followed.

perimental dependence of the second virial coefficient on temperature, as shown in Appendix IV.

TABLE XII

COMPARISON OF CORRECTED VALUES OF γ AND VALUES CALCULATED FROM EQUATION (62)

Press., atm.	$\gamma_{corr.}$	$\gamma_{calc.}$	$(\gamma_{corr.} - \gamma_{calc.}) \times 10^{-3}$
0.9951	1.647$_7$	1.6656	18
2.275	1.652$_5$	1.6650	13
5.283	1.659	1.6643	9
7.871	1.660	1.6636	3
9.861	1.662	1.6631	1
11.754	1.662$_5$	1.6626	0
13.800	1.668$_5$	1.6621	0
15.929	1.661$_5$	1.6616	0
17.623	1.661$_5$	1.6611	0
19.943	1.660	1.6605	0

The values calculated by means of Equation (62) are compared in Table XII to the experimental values used in deducing this equation. The excellent agreement above 10 atm. pressure shows that the accidental errors in this work are very small. Fig. 9 shows $\gamma_{exp.}$ and $\gamma_{corr.}$ as functions of the pressure. The three values by Jacyna, already referred to, were calculated from his
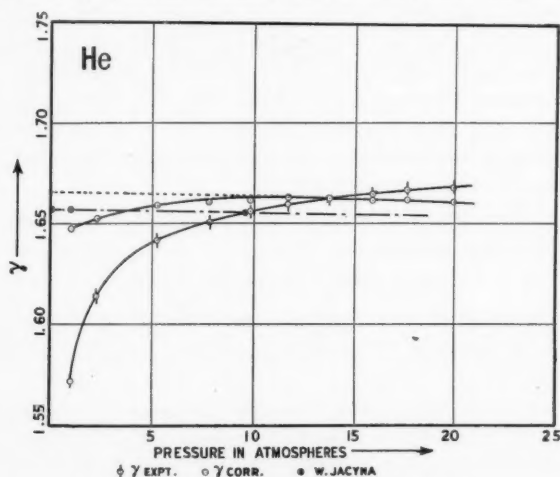

FIG. 9.   Values of γ for helium at 23.0° C.

published values of C_p and C_v. These values of Jacyna's work are listed in Table XIII and are compared to some from Equation (62) at the same pressure. It will be seen that they differ by about 0.5%, but both sets of results have almost identically the same pressure coefficient, which is negative.

The consistency with which results may be obtained by the resonance method is again demonstrated by the excellent agreement between the average of 17 values for helium at atmospheric pressure taken during 1938, while

the method was being developed, and the average of three values taken in June, 1939.

April and May, 1938: Average of 17 values, $\gamma = 1.647_3$
June, 1939: Average of 3 values, $\gamma = 1.647_7$

$\Delta\gamma$ is so large at low pressure that the values of γ found by experiment at these low pressures are misleading. Without the values at higher pressures, those at low pressure would be very unsatisfactory. A study of Table XI shows how important are the values at high pressure.

TABLE XIII

COMPARISON OF RESULTS OF JACYNA WITH THOSE OF THE AUTHORS

Press., kg./cm.²	W. Jacyna			Clark and Katz	Diff., %
	C_p	C_v	γ	γ calc.	
0	1.251	0.7550	1.657	1.6656	0.6
10	1.252	0.7563	1.653	1.6631	0.5

Accuracy

The errors are of two kinds,—constant errors (introduced in determining the constants of the apparatus), and accidental errors which vary from observation to observation. Further, there may be errors in auxiliary data, i.e., in the Pv data. The values of the apparatus constants have already been given.

The value of V_0 may contain an error due to the inequality of the volumes of the gas in the two chambers caused by a displacement of the piston from the middle position. If the volumes are unequal Equation (14) should be written

$$v = (\bar{v}_2 - \bar{v}_1) = -\frac{V_o' + V_o''}{V_o' V_o''} v_o ax.$$

The maximum possible displacement of the piston is about 1 mm., which would affect γ by about 0.015%. The departure from the middle position was always much less than this amount.

Accidental errors enter in the measurement of the frequency, in the location of the point of maximum amplitude and in the measurement of the pressure. The accuracy in these measurements is given as

Frequency to within	0.01%
Location of maximum amplitude	0.005%
Pressure to within	0.03%.

The high degree of precision with which values may be reproduced, as has been pointed out more than once, and the consistency with which the measurements at different pressures fall on smooth curves, are good indications that the errors are small.

That the errors arising from inaccuracies in the Pv data are small is shown by Table XIV in which are given calculations using data by different observers for hydrogen at 24.961 atm.

TABLE XIV

VALUES OF γ FOR HYDROGEN CALCULATED BY USE OF DIFFERENT Pv DATA

Source of Pv data	G	γ
Verschoyle	0.98685	1.409$_6$
Holborn and Otto	0.98549	1.410
Nijhoff and Keesom	0.98603	1.410$_6$

It will be seen that the differences are small, in no case over 0.07%. At lower pressures there is better agreement amongst the data, and the error is smaller.

Best Values of γ at Zero and 1 Atm. Pressure

Since the equations fitted to the experimental data give equal weight to all the measurements made on each gas, it is felt that the values given by these equations are relatively free of accidental errors, and are more accurate than the experimental values themselves.

The values at zero and 1 atm. pressure according to these equations are given in Table XV.

TABLE XV

COLLECTED VALUES OF γ AT ZERO AND 1 ATM. PRESSURE

Gas	Temp., °C.	0 press.	1 atm.
N_2	23.0	1.400$_3$	1.402$_4$
CO_2	23.8	1.294$_8$	1.300$_0$
H_2	24.4	1.403$_4$	1.403$_7$
A	24.2	1.666$_2$	1.669$_7$
He	23.0	1.665$_6$	1.665$_3$

Acknowledgments

References

1. BRODERSEN, P. H.   Z. Physik, 62 : 3-4; 180-187.   1930.
2. CLARK, A. L. and KATZ, L.   Can. J. Research, A, 16 : 183-189.   1938.
3. DEMING, W. E. and DEMING, L. S.   Phys. Rev. 56 : 108-112.   1939.
4. DEMING, W. E. and SHUPE, L. E.   Phys. Rev. 37 : 638-654.   1931.
5. DEMING, W. E. and SHUPE, L. E.   Phys. Rev. 40 : 848-859.   1932.
6. DEN HERTOG.   Mechanical vibrations.   McGraw-Hill Book Company, New York.   1934.
7. EUCKEN, A.   Handbuch der Experimentalphysik.   Vol. 8, Part 2.   W. Wien and F. Harms.   Leipzig.   1929.
8. HODGE, A. H.   J. Chem. Phys. 5 : 974-977.   1937.
9. HOLBORN and OTTO.   *In* Handbuch der Experimentalphysik, by A. Eucken.   Vol. 8, Part 2 : 167-178.   W. Wien and F. Harms.   Leipzig.   1929.
10. HUBBARD, J. C. and HODGE, A. W.   J. Chem. Phys. 5 : 978-979.   1937.
11. JACYNA, W.   Z. Physik, 92 : 661-674.   1934.
12. KIRCHHOFF.   *In* The specific heats of gases, by J. R. Partington and W. G. Shilling, p. 52.   Ernest Benn Ltd., London.   1924.
13. MICHELS, A. and MICHELS, C.   Proc. Roy. Soc. London, A, 153 : 201-214.   1935.
14. MICHELS, A. and MICHELS, C.   Proc. Roy. Soc. London, A, 160 : 348-357.   1937.
15. NIJHOFF, G. P. and KEESOM, W. H.   Commun. Phys. Lab. Leiden, 188d, 188e.   1928.
16. PARTINGTON, J. R. and SHILLING, W. G.   The specific heats of gases.   Ernest Benn Ltd. London.   1924.
17. RINKEL, R.   Physik. Z. 30 : 805.   1929.
18. RÜCHARDT, E.   Physik. Z. 30 : 58-59.   1929.
19. TRAVERS, M. W., SENTER, G., and JAQUEROD, A.   Phil. Trans. Roy. Soc. A, 200 : 105-180.   1903.
20. VERSCHOYLE, T. T. H.   Proc. Roy Soc. London, A, 111 : 552-576.   1926.
21. WORTHING, A. G.   Phys. Rev. 32 : 243-246.   1911.
22. WORTHING, A. G.   Phys. Rev. 33 : 217-267.   1911.

APPENDIX I

Solution for $\Delta \overline{T}$ for Non-adiabatic Compressions

To find $\Delta \overline{T}$ we equate the rate at which work is done on an element of gas to the rate at which it gains or loses heat and the rate at which its internal energy changes.

From the first law of thermodynamics

$$dQ = c_v dT + (\lambda + P)dv, \text{ per unit mass,} \qquad (63)$$

where

$$\lambda = \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P, \text{ the internal pressure,}$$

giving

$$\frac{dQ}{dt} = C_v \frac{dT}{dt} + (\lambda + P)\frac{dv}{dt}. \qquad (64)$$

The term, $\dfrac{dQ}{dt}$, the rate at which heat is exchanged with the surroundings, depends on the loss or gain of heat by conduction, convection, and radiation. The loss of heat by radiation is small, and we shall assume that we may also neglect the effects of convection. Then we may use the equation for the conduction of heat,

$$\frac{dQ}{dT} = k\nabla^2 T \text{ per unit volume}$$

$$= \frac{k}{\rho}\nabla^2 T \text{ per unit mass,} \qquad (65)$$

where k is the conductivity of the gas and $\rho = 1/v$, the density.

Combining (63) and (65) we get

$$\frac{k}{\rho}\nabla^2 T = C_v\left(\frac{dT}{dt}\right) + (\lambda + P)\frac{dv}{dt}. \qquad (66)$$

To proceed with the solution of this equation a few simplifying assumptions must be made. The rates of change dT/dt and dv/dt in this equation are important, whereas changes in C_v, ρ, P, λ, are of secondary importance, varying but little from their original equilibrium values, P_o, ρ_o, λ_o, C_{vo}. Further, to avoid the use of dv/dt, which is an unknown function of the co-ordinates, it may be replaced without serious error by $d\bar{v}/dt$, the derivative of the mean value.

Effecting these changes we get

$$\frac{k}{\rho_o}\nabla^2 T = C_{v_o}\frac{dT}{dt} + (\lambda_o + P_o)\frac{d\bar{v}}{dt}. \qquad (67)$$

Let us assume the solution of this equation to be

$$T = T_o - \frac{(\lambda_o + P_o)}{C_{v_o}}(\bar{v} - v_o) + \theta, \qquad (68)$$

where θ is an unknown function of the co-ordinates and time, expressing the

effect on T of non-adiabatic changes of volume. It actually measures the departure of T from a true adiabatic change.

Introducing (68) into (67) gives

$$\frac{\partial \theta}{\partial t} = \frac{k}{\rho_o C_{v_o}} \nabla^2 \theta = \alpha^2 \nabla^2 \theta . \tag{69}$$

$\Delta \overline{T}$ is found from Equation (68) by taking the mean values over the whole gas volume

$$\Delta \overline{T} = (\overline{T}_2 - \overline{T}_1) = (\overline{T}_2 - \overline{T}_o) - (\overline{T}_1 - \overline{T}_o),$$

where the subscripts refer to volumes 1 and 2.

When Equations (13) are combined with (68) and integrated over the volume we get

$$\left. \begin{aligned} \overline{T}_1 &\equiv T_o - \frac{\lambda_o + P_o}{C_{v_o}} \frac{v_o a x}{V_o} + \overline{\theta}_1 , \\ \overline{T}_2 &= T_o + \frac{\lambda_o + P_o}{C_{v_o}} \frac{v_o a x}{V_o} + \overline{\theta}_2 , \end{aligned} \right\} \tag{70}$$

where

$$\overline{\theta} = \frac{1}{V} \int \int \int \theta d\tau . \tag{71}$$

These last three equations give

$$\Delta \overline{T} = 2 \left(\frac{\lambda_o + P_o}{C_{v_o}} \right) \frac{v_o a x}{V_o} + \overline{\theta}_2 - \overline{\theta}_1 . \tag{72}$$

So far it has not been possible to solve completely Equation (69) for a cylinder of finite length with plane ends, because of the complicated boundary conditions. If, however, we assume the gas container to be spherical in shape, the solution is readily obtained.

Solution of Equation (69) for a Spherical Cavity

To obtain this solution the following conditions are assumed to apply:

(a) The compressions of the gas in the immediate vicinity of the walls are assumed to take place isothermally. Then by Equation (68)

$$\theta_1 = \frac{\lambda_o + P_o}{C_{v_o}} \frac{v_o}{V_o} a x = -\theta_2 , \qquad \text{at} \qquad r = b, \tag{73}$$

where r is the radius vector and b is the radius of the sphere.

(b) The temperature of the gas has spherical symmetry about the origin placed at the centre.

(c) The gas container is small compared with the wave-length of sound at the frequencies used (25 to 150 cycles per sec.), so that irregularities in temperature, pressure, and density due to the finite velocity of sound are small and of secondary importance compared to those caused by the loss of heat through conduction.

(d) To facilitate the solution of the spherical case, a new function μ will be introduced defined by

$$\theta = \frac{\mu}{r} . \tag{74}$$

Since $T \neq \infty$ at $r = 0$, then μ must be zero at the centre. This really amounts to assuming that the compressions at the centre are strictly adiabatic, which is reasonable.

Introducing Equation (74) into (69), transforming to spherical co-ordinates, and making use of assumption (b) we get

$$\frac{\partial \mu}{\partial t} = \alpha^2 \frac{\partial^2 \mu}{\partial r^2} . \tag{75}$$

The particular solutions of this equation obtained by assuming the variables to be separable as is universally done, are

$$e^{\pm \frac{r}{\alpha}\sqrt{\frac{\omega}{2}}} \frac{\sin}{\cos}\left(\omega t \pm \frac{r}{\alpha}\sqrt{\frac{\omega}{2}} + \nu \right), \tag{76}$$

where ν is a constant.

The general solution, formed to satisfy assumption (d) is then

$$\mu = A\left[e^{-\frac{r}{\alpha}\sqrt{\frac{\omega}{2}}} \sin\left(\omega t + \frac{r}{\alpha}\sqrt{\frac{\omega}{2}} + \nu \right) - e^{-\frac{r}{\alpha}\sqrt{\frac{\omega}{2}}} \sin\left(\omega t + \frac{r}{\alpha}\sqrt{\frac{\omega}{2}} + \nu \right)\right]. \tag{77}$$

Solutions for Constants A and ν

At the boundary, $r = b$, we have from Equations (73), (79), and (68),

$$\mu_1 = -\mu_2 = \left(\frac{\lambda_o + P_o}{C_{v_o}}\right) b \frac{v_o}{V_o} ax_m \sin \omega t = Sb \sin \omega t. \tag{78}$$

Solving gives

$$\text{Cos } \nu = \frac{A}{Sb} (e^{-n} - e^n) \cos n$$

$$\text{Sin } \nu = \frac{A}{Sb} (e^{-n} + e^n) \sin n \tag{79}$$

$$A^2 = \frac{S^2 b^2}{e^{2n} + e^{-2n} - \cos 2n} ,$$

where

$$n = \frac{b}{\alpha}\sqrt{\frac{\omega}{2}} . \tag{80}$$

Finally $\bar{\theta}$ is obtained by taking the mean integrated value over the gas volume as defined by Equation (71).

$$\bar{\theta} = \frac{1}{V}\iiint \theta d\tau = \frac{3}{4\pi b^2}\int_0^b \theta \, 4\pi r^2 dr = \frac{3}{b^2}\int_0^b \mu r \, dr. \tag{81}$$

Integrating and combining with (79) gives

$$\bar{\theta}_1 = \frac{3}{2n}\left(\frac{e^{2n} - e^{-2n} - 2\sin 2n}{e^{2n} + e^{-2n} - 2\cos 2n}\right) S \sin \omega t$$

$$+ \frac{3}{2n^2}\left(1 - n\frac{e^{2n} - e^{-2n} + 2\sin 2n}{e^{2n} + e^{-2n} - 2\cos 2n}\right) S \cos \omega t. \tag{82}$$

Calculations show that $2n > 24$ and since $2 \sin 2n \leq 2$, we may write

$$\bar{\theta}_1 = -\bar{\theta}_2 = \frac{3}{2n} S \sin \omega t + \frac{3}{2n^2} (1 - n) S \cos \omega t. \tag{83}$$

Substituting back for $S \sin \omega t$ as given by (78) and remembering that

$$x_m \cos \omega t = \frac{1}{\omega} \frac{d}{dt} (x_m \sin \omega t) = \frac{\dot{x}}{\omega} \tag{84}$$

we get

$$\bar{\theta}_2 - \bar{\theta}_1 = -\frac{3}{n} \left(\frac{\lambda_o + P_o}{C_{v_o}}\right) \frac{v_o a x}{V_o} - \frac{3}{\omega n^2} (1 - n) \left(\frac{\lambda_o + P_o}{C_{v_o}}\right) \frac{v_o a}{V_o} \dot{x} \tag{85}$$

giving

$$\Delta \bar{T} = 2 \frac{\lambda_o + P_o}{C_{v_o}} \frac{v_o a}{V_o} \left[\left(1 - \frac{3}{2n}\right) x - \frac{3}{2 \omega n^2} (1 - n) \dot{x}\right]. \tag{86}$$

From the well known thermodynamic equation

$$C_p - C_v = (P + \lambda) \left(\frac{\partial v}{\partial T}\right)_P \tag{87}$$

we have

$$\left(\frac{\lambda_o + P_o}{C_{v_o}}\right) = (\gamma - 1) \left(\frac{\partial \bar{T}}{\partial v}\right)_P . \tag{88}$$

So that finally

$$\Delta \bar{T} = 2(\gamma - 1) v_o \left(\frac{\partial \bar{T}}{\partial v}\right)_p \frac{a}{V_o} \left[\left(1 - \frac{3}{2n}\right) x - \frac{3}{2 \omega n^2} (1 - n) \dot{x}\right]. \tag{89}$$

APPENDIX II

Finite Amplitude of Oscillation

To solve Equation (9) it was assumed that the piston oscillations are of infinitesimal amplitude, so that we may write

$$\Delta \bar{P} = \left(\frac{\partial \bar{P}}{\partial T}\right)_v \Delta \bar{T} + \left(\frac{\partial P}{\partial v}\right)_T \Delta \bar{v} . \tag{90}$$

In this form, $\Delta \bar{P}$ reduces to a linear function of the piston displacement, so that Equation (4) can be readily solved.

The actual oscillations are, of course, of finite amplitude, and if the above assumption were not sufficiently correct, then the results would be affected in two ways.

(a) The solution for $\Delta \bar{P}$ would contain more terms and thus introduce other factors into the equation for γ.

(b) The reaction of the gas would no longer be proportional to the displacement, and the equation of motion could not be written in the simple form:

$$x = \frac{K'}{\sqrt{(\omega_n^2 - \omega^2)^2 + \beta'^2 \omega^2}} \sin \omega t . \tag{91}$$

This would mean that the method of calculation of ω_m by equation

$$\omega_m^2 = \frac{\omega_1^2 + \omega_2^2}{2} \tag{92}$$

would be open to question.   The reason for questioning the validity of this equation for ω_m is readily seen when the resonance curve of a forced harmonic system with a *non*-linear reaction is examined.   Fig. 10 is such a curve as given by Den Hertog (6).
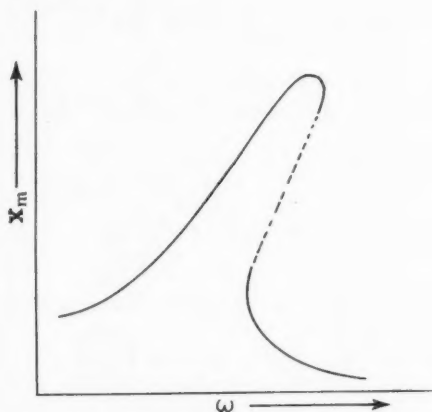

FIG. 10.   *Theoretical resonance curve with non-linear reaction.*

To meet the first point:

To estimate the magnitude of the change in γ when the amplitudes of oscillation are no longer considered infinitesimal, it will be sufficient, for simplicity, to assume the characteristic equation of state of the gas to be

$$Pv = RT, \tag{93}$$

giving

$$\overline{P}_1 = \frac{R\overline{T}_1}{v_1} \qquad \overline{P}_2 = \frac{R\overline{T}_2}{v_2} \tag{94}$$

and

$$\Delta\overline{P} = (\overline{P}_2 - \overline{P}_1) = R\left(\frac{\overline{T}_2}{\overline{v}_2} - \frac{\overline{T}_1}{\overline{v}_1}\right). \tag{95}$$

By Equation (13)

$$\overline{v}_1 = v_o\left(1 + \frac{ax}{V_o}\right) \qquad \overline{v}_2 = v_o\left(1 - \frac{ax}{V_o}\right). \tag{96}$$

Introducing (96) and (95) and setting

$$\Delta\overline{T} = \overline{T}_2 - \overline{T}_1, \quad \text{and} \quad \overline{T}_2 + \overline{T}_1 = 2T_o, \tag{97}$$

$$P = \frac{1}{1 - \left(\frac{ax}{V_o}\right)^2}\left\{\frac{R}{v_o}\Delta\overline{T} + 2P_o\frac{ax}{V_o}\right\}. \tag{98}$$

On the other hand, using Equation (90), obtained by assuming the amplitude of oscillation to be infinitesimal, and Equations (93) and (96)

$$\Delta\overline{P} = \left(\frac{R}{v_o}\Delta\overline{T} + 2P_o\frac{ax}{V_o}\right). \tag{99}$$

Thus it is seen that the above assumption of infinitesimal amplitude is equivalent to saying that the factor $\dfrac{1}{1 - \left(\dfrac{ax}{V_o}\right)^2} = 1$. Actually the magnitude of this factor is very close to unity. We have

$$a = 12.56 \text{ sq. cm.,}$$
$$V_o = 104.02 \text{ cc.,}$$
$$x_m = 0.07 \text{ cm. (max.)}$$

Then

$$\frac{1}{1 - \left(\dfrac{ax}{V_o}\right)^2} \leqq 1.00007.$$

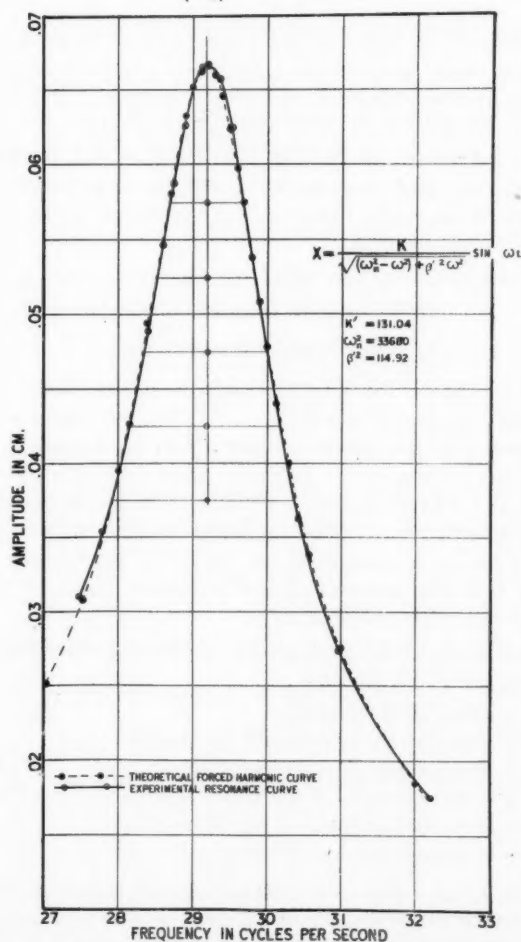

FIG. 11. *Comparison of actual and theoretical resonance curves.*

To meet the second point:

Expanding Equation (98) by Taylor's series gives

$$\Delta \overline{P} = \left(\frac{R}{v_o} \Delta \overline{T} + 2P_o \frac{a x}{V_o} \right) \left(1 - \left(\frac{a x}{V_o} \right)^2 \right)^{-1}$$
$$= \left(\frac{R}{v_o} \Delta \overline{T} + 2P_o \frac{a x}{V_o} \right) \left(1 + \left(\frac{a x}{V_o} \right)^2 + \left(\frac{a x}{V_o} \right)^4 + \dots \right). \quad (100)$$

Thus $\Delta \overline{P}$ would no longer appear to be a linear function in x; however, since calculations show $\left(\frac{a x}{V_o} \right)^2$ is very small, the terms in the expansion, except for the first, are all very small and the relationship between ΔP and x is very nearly linear.

A further check on the effect of the higher power terms in this expansion on the resonance curve was obtained by plotting a large-scale graph of the results of one of the experiments and superimposing on it the theoretical resonance curve obtained with linear reaction (Fig. 11).

The excellent agreement of these graphs shows that Equation (91) represents the actual resonance curve to a high degree of accuracy.* It is to be noticed that there is no visible "leaning over" of the resonance curve as would result from non-linear reaction.

APPENDIX III

Mounting of Resonator

It can be shown that if the resonator is so mounted that it can vibrate as a whole with some natural frequency ω_r, and if conditions are such that the resonance frequency of the piston is lower than ω_r, this point of resonance is displaced to a lower frequency. If, on the other hand, the point of resonance of the piston is at a frequency higher than ω_r, the point of resonance is displaced to a higher frequency. The resonator must therefore be so mounted that its natural period is outside of the region of frequencies used, and all factors causing this displacement of the resonance point of the piston are such as to make this effect a minimum.

For purposes of analysis the apparatus may be represented by an equivalent set-up as shown in Fig. 12, where

$$m = \text{mass of the piston}$$
$$k = \text{reaction to compression by the gas}$$
$$\beta = \text{friction factor acting on the piston}$$
$$M = \text{effective mass of the whole system}$$
$$K = \text{effective stiffness of the mounting}$$
$$B = \text{effective friction of mounting}$$

---

* The maximum difference between the calculated and the experimentally determined amplitudes on the graph as measured on the large scale plot was less than 0.0007 cm. As the experimental amplitudes were measured to ±0.0005 cm., the agreement may be considered to be within experimental error.
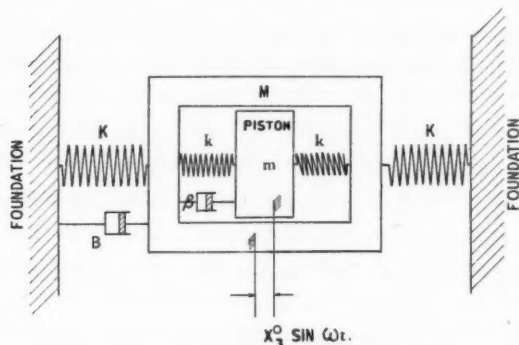
FIG. 12. *Elementary diagram of mounting.*

and $x_3^\circ \sin \omega t$ is the driving force acting between m and M. If the piston m moves a distance x_1 in the positive direction with the reaction causing M to move a distance x_2 in the opposite direction then

$$m\ddot{x}_1 + \beta(\dot{x}_1 - \dot{x}_2) + k(x_1 - x_2) = x_3^\circ \sin \omega t \tag{101}$$

$$M\ddot{x}_2 + B\dot{x}_2 + \beta(\dot{x}_2 - \dot{x}_1) + Kx_2 + k(x_2 - x_1) = -x_3^\circ \sin \omega t. \tag{102}$$

Solving gives x_1 and x_2 as functions of ωt and the constants of the systems. In particular, if x_1° and x_2° are the maximum amplitude,

$$x_2^\circ = \frac{R}{\sqrt{\left(1 - \dfrac{\omega_r^2}{\omega^2}\right)^2 + \dfrac{L^2}{\omega^2}}} \, x_1^\circ, \tag{103}$$

where $\qquad R = m/M, \qquad L = B/M, \qquad w_r = K/M. \tag{104}$

By differentiating (103) and equating to zero, the frequency at which the ratio of x_2° to x_1° is a maximum is found to be

$$\omega^2 = \frac{\omega_r^4}{\omega_r^2 - \dfrac{L^2}{2}} . \tag{105}$$

Combining with Equation (100)

$$\xi = (x_2^\circ/x_1^\circ)_{\text{max.}} = \frac{1}{\sqrt{1 + \dfrac{L}{2}\left\{\dfrac{1}{2} - \dfrac{1}{\omega_r^2}\right\}}} \, \frac{\omega_r}{L} \, R . \tag{106}$$

Neglecting $\dfrac{1}{\omega_r^2}$ as compared to $\frac{1}{2}$ and combining with (104)

$$\xi = \frac{1}{\sqrt{1 + \dfrac{L^2}{4}}} \cdot \frac{\omega_r}{L} \cdot \frac{m}{M} . \tag{107}$$

Since the resonance of the piston is very sharp, x_1° is appreciable only near its point of resonance, and, since L is generally small as compared to ω_r,

the ratio ξ has its maximum by Equation (105) at about $\omega = \omega_r$. Thus the region in which this disturbing effect is most pronounced is when both x_1° and ξ have maxima at the same frequency, that is, when the resonance of the piston falls in the neighbourhood of ω_r. The magnitude of ξ as given by (107) varies as $\dfrac{\omega_r m}{L M}$. If this factor is kept small the vibrations of the system will be small even when conditions are most favourable for maximum disturbance.

In accordance with the above considerations the apparatus was fastened to a concrete pier, and further to increase its effective mass M, it was bolted to a 150 lb. block of lead imbedded in the concrete and a 130 lb. block of lead (weight W in Fig. 4) fastened to the lifting magnet. These changes shifted the natural period of the mounting to over 200 cycles per sec. and reduced the vibrations of the apparatus to a point where they could be barely felt, even when the piston was made to oscillate with an amplitude three or four times larger than that for normal operations.

APPENDIX IV

That the extrapolation used in determining low values of γ for low pressures is justifiable is seen from the following.

For low pressure we may write without serious error [see Equation (46)]

$$PV = RT + BP .$$

We have then

$$V = \frac{RT}{P} + B \quad \text{and} \quad P = \frac{RT}{V - B} . \tag{108}$$

Then $\gamma = \dfrac{C_p}{C_v}$ and the slope of the γ-P line at constant temperature

$$\left(\frac{\partial \gamma}{\partial P}\right)_T = \frac{1}{C_v}\left(\frac{\partial C_p}{\partial P}\right)_T - \frac{\gamma}{C_v}\left(\frac{\partial C_v}{\partial P}\right)_T . \tag{109}$$

From thermodynamics we have

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad \text{and} \quad \left(\frac{\partial C_v}{\partial P}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v\left(\frac{\partial V}{\partial P}\right)_T , \tag{110}$$

since B is a function of T alone,

so

$$\left(\frac{\partial \gamma}{\partial P}\right)_T = 2\gamma\frac{dB}{dT} + (\gamma - 1)\frac{T}{C_v}\frac{d^2B}{dT^2} + \frac{2\gamma}{C_v R}\left(\frac{dB}{dT}\right)^2 P , \tag{111}$$

which is linear in P. Now these various derivatives are all small quantities, so, unless P is large, the last term may be neglected, when the slope of the γ-P line is constant and the line is straight. If this term cannot be neglected the equation of the γ-P line is a parabola as shown for carbon dioxide

(see Fig. 6).   Of course if the equation of the isothermal is not given by the two terms used and higher powers of P appear, the equation of the γ-P line is of an order higher than the second.

For the nearly perfect gases, helium, hydrogen, nitrogen, argon, etc., the lines are straight, as shown on the graphs, while the second degree equation for carbon dioxide is realized.

It is not to be expected that peculiarities will appear at low pressures, for as the pressure is made lower and lower the above holds more and more rigidly.

Then
$$\lim_{P=0} \left(\frac{\partial \gamma}{\partial P}\right)_T = 2\gamma \frac{dB}{dT} + (\gamma - 1)\frac{T}{C_v}\frac{d^2B}{dT^2} \tag{112}$$

gives the slope of the γ-P line at zero pressure which in the case of helium was found to be negative.
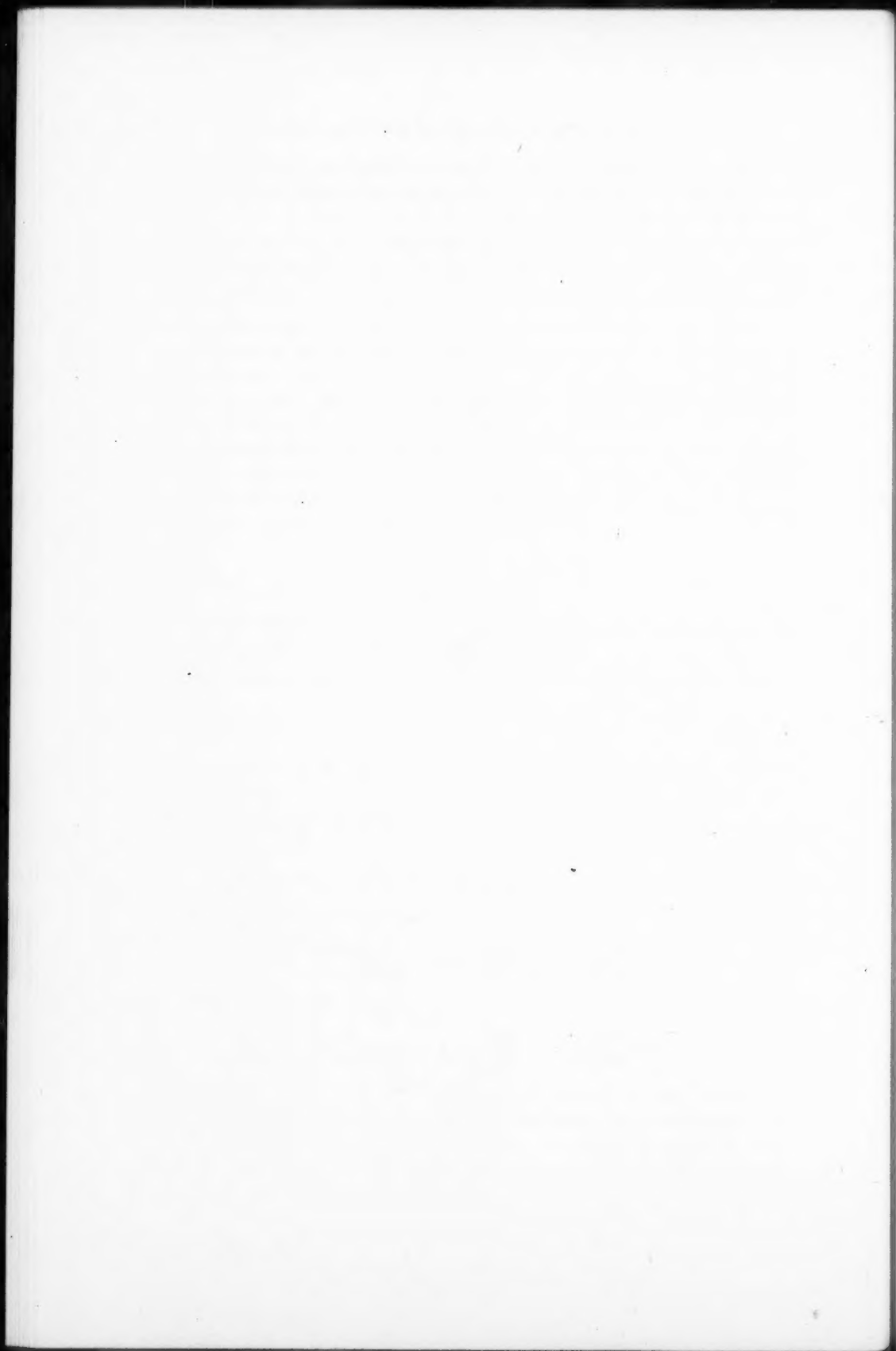
THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXIV. *CORYDALIS OCHOTENSIS* TURCZ.[1]

BY RICHARD H. F. MANSKE[2]

Abstract

The alkaloids of *Corydalis ochotensis* consist of four known bases, namely, protopine, cryptocavine, ochotensine, and aurotensine, together with two new ones, namely, ochotensimine (F48) and alkaloid F49. Ochotensimine is the O-methyl ether of ochotensine. It has not been obtained crystalline, but it has been characterized as the methiodide and the derived dihydro-methine base. In addition to acetyl-ornithine, the isolation of which has already been recorded, fumaric acid and maltol were also found.

Corydalis ochotensis Turcz. is of interest in that it is the first plant from which an acylated amino acid, namely acetyl-ornithine, has been isolated (3).* The finding of such a substance was admittedly fortuitous, and it was encountered while the plant was under investigation for its alkaloids. The present paper deals with the latter.

It is hardly necessary to note that protopine was present in quantity, but in this case it was accompanied by appreciable amounts of cryptocavine (F34), first found in *Dicentra chrysantha*. Another alkaloid of more than passing interest is one now termed ochotensimine (F48). Neither the free base nor any of its salts has been obtained in a crystalline condition, but the methiodide crystallizes with great facility. The last proved to be identical with the methyl-ether methiodide of ochotensine. Ochotensimine is therefore ochotensine O-methyl-ether. The plant in question is also the best source of ochotensine (F17) which was recorded as having the empirical formula $C_{21}H_{21}O_4N$, and this seems to be confirmed by the analyses of a number of derivatives. Two other phenolic alkaloids, namely aurotensine and an unidentified base, alkaloid F49, were isolated in small amounts. These alkaloids, six in number, were the only ones found, but the plant, while elaborating only comparatively few individuals, elaborates some of them in appreciable amounts.

A neutral substance, not met before in this series of investigations, was present in traces. It gave analytical figures in agreement with those for

maltol.   An authentic specimen of the latter was not available so that a direct comparison could not be made.   Feuerstein (1) isolated maltol from the needles of *Abies pectinata* D.C. (*A. alba* Mill.), but an attempt to isolate it from the needles of *Pinus strobus* L. collected in July did not yield it.   In view of the identity of melting points and chemical reactions there seems to be, however, no doubt that the substance isolated is in fact maltol.

Experimental

There was available a total of 43.2 kg. of dried material of which the first year's tap roots constituted 15.5 kg.   The aerial portion included not only that collected from the first year's growth but 9.6 kg. of second year's growth collected when the plant was in flower.   It is felt that any alkaloids likely to be elaborated by the plant at any stages of growth were present in these materials.   The various collections were examined separately, but no significant differences except quantitative ones were observed.

The separation of the alkaloids was carried out by means of the author's standardized procedure.   The following is a summary:

Base hydrochlorides extracted from aqueous solution by means of chloroform,

> BC—Non-phenolic bases,—ochotensimine (F48), cryptocavine.
> EC—Phenolic bases extracted from alkaline solution by means of ether,—ochotensine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform,

> BS—Non-phenolic bases,—protopine, cryptocavine.
> BSE and EES—Phenolic bases precipitated by carbon dioxide,—aurotensine, alkaloid F49.

Ochotensimine and *Cryptocavine*

The fraction (BC) after washing and drying was suspended in hot methanol until mostly dissolved, allowed to cool, and filtered.   The insoluble portion consisted of ochotensine which, though phenolic, is only moderately soluble in alkaline solutions.   The filtrate was again filtered with the aid of charcoal and evaporated to a thin syrup.   In the course of several days a small crop of crystals had separated.   When recrystallized from chloroform-methanol the alkaloid melted at 223° C.*, and in admixture with a specimen of cryptocavine from *Fumaria officinalis* it melted at the same temperature.

The alkaloids in the mother liquor, from which the cryptocavine had been obtained, were redissolved in dilute oxalic acid, and the filtered solution exhausted with ether and then basified with an excess of potassium hydroxide. The liberated bases were extracted with ether and the solution was washed with water and dried over potassium hydroxide.   Removal of the solvent left a viscous resin which, in contact with ether-methanol, deposited only a small amount of cryptocavine.   The base was purified further by converting it into the hydrochloride and re-extracting the latter from an aqueous solution

* *All melting points are corrected.*

by means of chloroform.   The regenerated base then consisted of a honey-coloured resin that did not crystallize in contact with a number of solvents in the course of two years.   The picrate is sparingly soluble and amorphous. Neither the *d*- nor the *l*-tartrate, nor a number of other salts, could be obtained crystalline.   This base, which is substantially pure ochotensimine, readily yields a crystalline methiodide when its solution in ether-methanol is treated at room temperature with methyl iodide.   When washed with methanol and then with ether the methiodide melts with previous decomposition at 225° C. $[\alpha]_D^{22} + 49.2°(c = 0.2$ in methanol).

The methylation of ochotensine proceeded only very slowly when its suspension in chloroform-methanol was treated with an ethereal solution of diazomethane.   Repeated evaporation and the addition of fresh diazomethane finally converted most of the alkaloid into a non-phenolic base which thus far could not be crystallized.   The methiodide, prepared as above, melted at the same temperature, and admixture of the two did not depress the melting point.   Seeding of a supersaturated methanolic solution of the methiodide from one source with a crystal from the other source induced immediate crystallization. $[\alpha]_D^{22} +44.0$ ($c = 0.2$ in methanol).   Found: C, 52.97; H, 5.36; N, 2.43; OMe, 11.93; I, 23.94%*.   Calc. for $C_{22}H_{23}O_4N$: $CH_3I . H_2O$; C, 52.47; H, 5.32; N, 2.66; 2OMe, 11.79; I, 24.13%.

When ochotensimine methiodide, either in aqueous or absolute methanolic solution, is treated with potassium hydroxide it rapidly decomposes, yielding an insoluble non-basic resin.   It was possible, however, to prepare a dihydromethine base by Emde's reduction scission.   The products from natural ochotensimine and from O-methylated ochotensine were identical.

A cooled aqueous solution of ochotensimine methiodide (2 gm.) in water was treated with 100 gm. of 2.5% sodium amalgam.   The aqueous solution was stirred vigorously and maintained just acid by the slow addition of hydrochloric acid.   When the sodium had been used up, the filtered aqueous solution was basified with ammonia and the liberated base extracted with ether..   The extract was evaporated to a thin syrup and the base that separated was recrystallized from dry ether.   It melted sharply at 92° C.   Calc. for $C_{23}H_{27}O_4N$: C, 72.44; H, 7.09; N, 3.68; 2OMe, 16.27%.   Found: C, 72.73; H, 7.01; N, 3.68; OMe, 16.28%.

This substance, which is probably ochotensimine dihydromethine, yields a hydrochloride that is sparingly soluble in water.

Ochotensine

Ochotensine is only very sparingly soluble in ether, and therefore its extraction from the alkaline solution is tedious though virtually complete.   It was found advantageous to treat the alkaline solution with hydrochloric acid until it was just alkaline to litmus and filter off the crystalline ochotensine thus obtained.   The remainder in the filtrate was recovered by extraction with ether.   Purification was effected by redissolving in dilute hydrochloric acid

---

* *All analyses are the means of satisfactory duplicates.*

and slowly precipitating the warm solution with ammonia. It was thus obtained in almost colourless prisms that melted at 248° C., and when this product was recrystallized from a large volume of boiling chloroform it consisted of brilliantly colourless prisms melting at 252° C. In admixture with alkaloid F17 from *C. sibirica* (1) it melted at 251 to 252° C. $[\alpha]_D^{24} +51.7°$ ($c = 0.2$ in chloroform) $[\alpha]_D^{23} +63.9$ ($c = 2.0$ in $0.1N$ HCl).

The yield from the roots was less than 0.001%. The first year's leaves yielded 0.06% and the second year's aerial portion yielded 0.10%.

Protopine and Cryptocavine

The dried fraction (BS) was dissolved in chloroform and the filtered solution evaporated to a thin syrup. The addition of methyl alcohol and a nucleus of protopine induced immediate crystallization. The protopine was purified by recrystallization from chloroform-methanol; the product, combined with some base recovered from the mother liquors, gave a yield of 0.37% from the roots. The aerial portion contained only about 0.1% protopine, but the amount of cryptocavine was much larger than in the roots.

In general the cryptocavine did not contaminate the protopine when the latter was crystallized rapidly and then filtered off. The filtrate was largely freed of solvent and the residue dissolved in hot dilute hydrochloric acid, and the solution slowly evaporated until protopine hydrochloride began to crystallize. On cooling, a mixture of protopine and cryptocavine hydrochlorides separated. The mixture was rapidly warmed to dissolve the more soluble cryptocavine salt and then filtered. On cooling, the filtrate deposited the latter in fragile elongated plates that were filtered off before some protopine salt also crystallized. (The ultimate filtrate yielded further amounts of protopine and a mother liquor from which a little more cryptocavine hydrochloride could be crystallized.) The hydrochloride was dissolved in warm water and the free base precipitated by adding an excess of potassium hydroxide. After filtering, washing, and drying, the base was dissolved in chloroform and the filtered solution evaporated to a thin syrup. The addition of methanol induced the almost immediate crystallization of colourless fine needles that melt sharply at 223° C. Admixture with specimens of cryptocavine from other sources did not lower the melting point. The yield of this alkaloid from the second year's growth of the plant was 0.03%.

Aurotensine and Alkaloid F49

The fractions (BSE and EES) were dissolved in methanol and the filtered solution was neutralized with methanolic hydrogen chloride. It was then evaporated to a thin syrup and repeatedly evaporated with chloroform, and the thin syrup washed with dry ether. The syrup was dissolved in methanol and treated with ethyl acetate until the incipient turbidity just disappeared on mixing. The crystals of a hydrochloride that slowly separated in the course of several days proved to be those of aurotensine (F18). A small portion of the salt was dissolved in hot water and the rapidly cooled solution basified with ammonia. The liberated base was extracted with ether and the residue

from the extract dissolved in a small volume of methanol. The addition of dry ether induced the crystallization of almost colourless elongated tablets that melt with effervescence at 126 to 127° C. Admixture with a specimen of aurotensine from *C. aurea* did not lower the melting point. Aurotensine dissolved in cold sulphuric acid to a colourless solution that becomes brilliantly green on gentle warming and deep purple on further heating. The yield was somewhat less than 0.003%. The filtrate from which no more aurotensine hydrochloride could be crystallized was diluted with water and the organic solvents were boiled off. The filtered aqueous solution was basified with ammonia and extracted with ether. The ether solution was thoroughly washed with water and evaporated somewhat. It was then filtered with the aid of charcoal and evaporated to a resin. The resin when dissolved in methanol slowly deposited a small amount (0.05 gm. from 43 kg.) of base in colourless prisms that was recrystallized from boiling methanol, in which it is only sparingly soluble. Alkaloid F49 as thus obtained melts with decomposition at 228° C. when placed in the bath at 205° C. On gentle warming, a solution of the alkaloid in sulphuric acid becomes violet, which turns to reddish-purple on further heating. Analyses indicate the formula $C_{19}H_{23}O_4N$ containing one methoxyl group. Found: C, 69.21; H, 7.04; N, 4.32; OMe, 9.94%. Calc. for $C_{19}H_{23}O_4N$: C, 69.72; H, 7.03; N, 4.28; 1OMe, 9.48%.

Maltol

The fraction (LC) consisted largely of fumaric acid and a substance that sublimed readily into the neck of a flask when the crude mixture was heated on a steam bath. Fraction (EEC) from the roots and aerial portion also yielded the same substance. It was recrystallized from methanol-ether and resublimed. As thus obtained it melted sharply at 162° C. Maltol ($C_6H_6O_3$) is stated to melt at 159° C. (? corr.). It gave the following reactions which are characteristic of maltol; ferric chloride in methanol,—deep violet colour; Fehling's solution,—reduction; ammoniacal silver nitrate,—reduction to silver mirror. Found: C, 57.55; H, 4.98%. Calc. for $C_6H_6O_3$: C, 57.14; H, 4.76%.

References

1. FEUERSTEIN, W. Ber. 34 : 1804-1806. 1901.
2. MANSKE, R. H. F. Can. J. Research, B, 14 : 354-359. 1936.
3. MANSKE, R. H. F. Can. J. Research, B, 15 : 84-87. 1937.

THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXV. *CORYDALIS PALLIDA* PERS.[1]

By Richard H. F. Manske[2]

Abstract

In addition to corypalline, the isolation of which has already been recorded, *Corydalis pallida* Pers. has yielded five known and two new alkaloids. The known bases are,—protopine, *d*- and *dl*-tetrahydro-palmatine, capaurine, and capauridine. The new alkaloids are capaurimine (F50), $C_{20}H_{23}O_5N$ (phenolic; two hydroxyl and three methoxyl groups), and alkaloid F51, $C_{20}H_{23}O_4N$ (one hydroxyl and three methoxyl groups). Capaurimine on methylation yields capaurine O-methyl ether, the *dl*- form of which is identical with capauridine O-methyl ether. Alkaloid F51 on methylation yields *dl*-tetrahydro-palmatine but it is not identical with the known *dl*-bases of the same formula.

The alkaloids of *Corydalis pallida* Pers. in their variety present a picture analogous to that of *C. aurea* (2). The author has in his possession fractions of the latter, which, in spite of numerous efforts, have not yet been crystallized, and the same is true of *C. pallida*. Nevertheless some eight alkaloids have been isolated and most of these have been adequately characterized or identified with known bases. Protopine, *d*-tetrahydro-palmatine and the *dl*-form of the latter constitute the only non-phenolic bases isolated thus far. It may be pointed out that in *C. aurea* the *dl*-base is accompanied by a preponderating amount of *l*-tetrahydro-palmatine. It is pertinent to note here too that alkaloid F27 (4) from *C. aurea* is in fact not quite pure *dl*-tetrahydro-palmatine.

The phenolic alkaloids definitely characterized include corypalline, which has been described (3, 4), the isomeric pair, capaurine and capauridine, and two new bases, capaurimine (F50) and alkaloid F51. It has now been found that capauridine as well as its methyl ether are optically inactive and that the latter is identical with racemized capaurine methyl ether. Racemization was effected by iodine oxidation and subsequent reduction, a procedure generally useful in the tetrahydro-protoberberine bases, and there is little question but that capaurine belongs to the same type. Capaurimine is closely related to capaurine. It is best represented by $C_{20}H_{23}O_5N$, it possesses only three methoxyl groups, and on methylation with diazomethane it yields capaurine O-methyl ether. Alkaloid F51 was closely associated with capaurimine. On methylation with diazomethane it yielded *dl*-tetrahydro-palmatine. Its low melting point (171° C.) alone indicates that it is not identical with either *dl*-corypalmine (m.p. 218° C.) or *dl*-isocorypalmine (m.p. 223° C.) (1). It is however isomeric with these bases and like them contains three methoxyl groups.

Experimental

The material for the present investigation was grown in a local garden. Most of it consisted of the first year's growth but some was collected from the second season's growth before and at maturity of the plants. Whenever feasible the author has examined a composite sample so that all the alkaloids elaborated by the particular plant at all stages of its growth would be present. There was available a total of 7.2 kg. of dried material of which the roots constituted only 450 gm.

The following is a summary of the alkaloids together with the fractions from which they were isolated.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—*d*- and *dl*-tetrahydro-palmatine.
BCE and EEC—Phenolic bases precipitated from alkaline solution by carbon dioxide,— capaurine, capauridine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine.
ES—Phenolic bases extracted from alkaline solution by means of ether,—capaurimine (F50).
BSE—Phenolic bases precipitated from alkaline solution by carbon dioxide,—capaurimine, alkaloid F51.
EES—Phenolic bases extracted from the bicarbonate solution by means of ether,— corypalline.

d- and dl-Tetrahydro-palmatine

The fraction (BC) was redissolved in dilute hydrochloric acid and the hot filtered solution partly cooled. The sparingly soluble hydrochloride which separated was recrystallized from much hot water and then converted to free base. The latter was recrystallized from methanol; it then melted at 151° C.* either alone or in admixture with a specimen of *dl*-tetrahydro-palmatine.

A second crop of hydrochlorides was obtained from the mother liquor and this proved to be a mixture of *d*- and *dl*-tetrahydro-palmatine. The bases from the mother liquor were regenerated by means of ammonia and recrystallized several times from methanol. The alkaloid thus obtained melted at 142° C. and admixture with an authentic specimen of *d*-tetrahydro-palmatine did not lower the melting point. The author is greatly indebted to Prof. Ernst Späth of the University of Vienna for a specimen of the latter. It may be noted that mixing with *l*-tetrahydro-palmatine yielded a mixture which melted indefinitely at 137° C. $[\alpha]_D^{24}$ +281° (c = 1.0 in methanol).

Capaurine and Capauridine

The fraction (BCE) was extracted with hot methanol and the filtered solution added to the ether extract (EEC). The sparingly soluble base which then crystallized was recrystallized from chloroform-methanol. The colourless fine

---

* *All melting points are corrected.*

needles thus obtained melted at 207° C.   In admixture with a specimen of capauridine from *C. aurea* there was no depression in melting point.

The filtrate from the capauridine yielded no further crystals on standing. The material was dissolved in dilute acid, the filtered solution basified with ammonia, and extracted with ether.   The washed extract was evaporated to dryness and the residue dissolved in methanol.   The base which then separated was recrystallized from hot methanol.   It melted at 164° C. either alone or in admixture with a specimen of capaurine from *C. aurea*.

Protopine

The fraction (BS) yielded only protopine although an exhaustive search for other bases was made.   It was readily obtained in a pure state (m.p. 210° C.) but the plant yielded only 0.014%.

Capaurimine

The fraction (ES) is always contaminated with some protopine and other non-phenolic bases when present in the plant.   It was therefore redissolved in dilute hydrochloric acid and the filtered solution basified with excess potassium hydroxide.   The alkaline filtrate from this was saturated with carbon dioxide and the precipitate filtered off, washed, and dried.   It was recrystallized first from methanol and then from chloroform-methanol.   The dense aggregates of colourless fine needles thus obtained melted at 212° C. to a brown liquid, some darkening taking place at 195° to 200° C.   This alkaloid, for which the name capaurimine (F50) is proposed, dissolves in sulphuric acid to yield a colourless solution which, on heating, merely became brown. $[\alpha]_D^{24}$ $-287°$ ($c = 0.4$ in chloroform).   Found: C, 67.10, 67.19; H, 6.63, 6.62; N, 3.88, 3.86; OMe, 26.99, 26.98%.   Calc. for $C_{20}H_{23}O_5N$: C, 67.23; H, 6.44; N, 3.92; 3OMe, 26.05%.

A small portion of capaurimine (0.1 gm.) was dissolved in methanol and treated with an ethereal solution of diazomethane.   The non-phenolic base isolated from the reaction mixture was crystallized first from ether and then from methanol.   It melted sharply at 150° C.   Capaurine O-methyl ether, when recrystallized from methanol, melts at 150° C. and a mixture of the two also melted at the same temperature.   A supersaturated methanolic solution of one substance was brought to immediate crystallization by inoculating with the other.

Alkaloid F51 and Capaurimine

Fraction (BSE) in methanol was neutralized with hydrochloric acid and the solution evaporated to a thin syrup.   The slow addition of acetone induced the crystallization of a sparingly soluble hydrochloride.   It was filtered off, washed with some methanol and then with acetone.   An aqueous solution of the salt was then basified with ammonia and the liberated base extracted with ether.   The washed ethereal extract was evaporated to a small volume and treated with enough methanol to dissipate the turbidity.   The base which then crystallized was washed with ether.   Alkaloid F51 as thus obtained consists of colourless fine prisms which melted at 171° C.   Found: C, 69.91, 70.04;

H, 6.82, 6.71; N, 4.09; 3.90; OMe, 26.66, 26.25%. Calc. for $C_{20}H_{23}O_4N$: C, 70.38; H, 6.75; N, 4.10; 3OMe, 27.27%.

A small quantity was methylated in methanolic solution by means of ethereal diazomethane. The non-phenolic product was recrystallized from ether containing a little methanol. It was obtained in colourless stout prisms which, either alone or in admixture with a specimen of *dl*-tetrahydro-palmatine, melted at 150° C.

The methanol-acetone mother liquor from which the above hydrochloride had been obtained was diluted with water and the organic solvents were boiled out. The filtered aqueous solution was basified with ammonia and extracted with ether. Distillation of the ether yielded a resin which crystallized readily in contact with methanol. The base was recrystallized from chloroform-methanol; it then melted at 212° C. It proved to be identical with capaurimine obtained from fraction (ES).

Corypalline

The dried residue representing fraction (EES) was extracted with several successive portions of boiling purified ether. The combined extract was evaporated to a small volume and treated with sufficient methanol to yield a clear solution. The base which then crystallized, was recrystallized by adding dry ether to a concentrated methanolic solution. It consisted of brilliant colourless needles which melted at 168° C.

The yields of alkaloids from this plant are difficult to state in precise terms because of the many operations entailed in their isolation. None of the phenolic bases were obtained in more than 0.02% yield. The mixture of tetrahydro-palmatines was isolated to the extent of approximately 0.5%.

References

1. GADAMER, J., SPÄTH, E., and MOSETTIG, E. Arch. Pharm. 265 : 675-684. 1927.
2. MANSKE, R. H. F. Can. J. Research, 9 : 436-442. 1933.
3. MANSKE, R. H. F. Can. J. Research, B, 15 : 159-167. 1937.
4. MANSKE, R. H. F. Can. J. Research, B, 16 : 81-90. 1938.

THE HETEROGENEOUS CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN HEAVY WATER[1]

By P. A. Giguère[2] and O. Maass[3]

Abstract

The catalytic decomposition of hydrogen peroxide dissolved in heavy water, both on the surface of glass in alkaline medium and on metallic gold, was measured at 35° C. The results, compared with those obtained under similar conditions for hydrogen peroxide in ordinary water, indicate that deuterium peroxide (D_2O_2) is much more stable than ordinary hydrogen peroxide towards such catalysts. The experimental results in both cases are of interest chiefly for comparison, and further investigations will be necessary before any sound conclusion can be drawn regarding the mechanism of the reactions involved.

Introduction

As a preliminary in a series of investigations on the properties of deuterium peroxide, it was felt necessary to obtain some information regarding the stability of this isotopic molecule as compared with that of hydrogen peroxide. The only data available at that time on this subject were those of Abel, Redlich, and Stricks (1, 2), who measured the iodine-catalysed decomposition of deuterium peroxide at 25° C. They found that the rate of decomposition was about 30% slower than in the case of hydrogen peroxide. A subsequent investigation by Oliveri-Mandalà and Indovina (6) on the influence of small quantities (1 to 5%) of heavy water on the catalytic decomposition of hydrogen peroxide in very dilute solutions (about 1 to 5%) by colloidal platinum seemed to indicate a still greater difference in stability between the two isotopic molecules. From these results it could be expected that strong solutions of deuterium peroxide would decompose on standing much more slowly than those of hydrogen peroxide. The availability of pure concentrated solutions of hydrogen peroxide in this laboratory offered an opportunity to test this assumption.

Catalytic Decomposition on Glass

As is well known, aqueous solutions of hydrogen peroxide kept in glass containers decompose on standing,

$$H_2O_2 = H_2O + \tfrac{1}{2}O_2 .$$

This is due mainly to the fact that the surface of the glass is slowly attacked, the alkali thus dissolved promoting the decomposition of the peroxide. This reaction, which has been shown by Rice (7) to be heterogeneous, was well suited for the investigation of the keeping properties of deuterium peroxide.

Since pure inhibitor-free solutions kept in Pyrex flasks decompose very slowly, a definite amount of alkali was added to the solutions in all cases to obtain reasonable reaction rates. The solutions of hydrogen peroxide used were prepared by vacuum distillation and evaporation of a 30% commercial solution containing no inhibitor. The reaction mixtures consisted of 2 cc. of 94% hydrogen peroxide and 3 cc. of either 95% deuterium oxide or redistilled water. These were contained in Pyrex test tubes immersed in a thermostat kept at 35° ± 0.05° C. Special care was exercised in cleaning the test tubes since the reaction velocity was found to depend a great deal on the condition of the glass surface. First, they were cleaned thoroughly in hot chromic acid, then washed repeatedly in distilled water, dried in vacuo and finally strongly heated in the flame of a Méker burner. During the course of the reaction the tubes were kept stoppered with waxed corks fitted with a capillary glass vent for the escape of the evolved oxygen. After the reaction mixture had warmed up to the temperature of the bath, 0.4 cc. of a 0.1 N solution of sodium hydroxide was added through a calibrated pipette and the well mixed solution was quickly analysed. This result was taken as the initial concentration, a.

<div align="center">TABLE I</div>

RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE ON GLASS IN THE PRESENCE OF ALKALI

Time, hr.	$a - x$, moles of H_2O_2	K	Time, hr.	$a - x$, moles of H_2O_2	K
In ordinary water					
	Run 1			Run 3	
0	12.65	—	0	12.65	—
2	10.3	1.33	2	9.7	1.31
4	7.4	1.34	4	6.9	1.51
6	5.0	1.54	6	4.45	1.72
8	3.0	1.81	8	2.9	1.95
		Av. 1.50			Av. 1.62
In heavy water					
	Run 2			Run 4	
0	12.65	—	0	12.65	—
2	11.65	0.412	4	10.85	0.378
6	10.35	0.332	8	9.9	0.308
8	9.6	0.345	12	8.45	0.334
10	9.05	0.334	24	5.4	0.355
13	8.25	0.329	28	4.8	0.343
22	5.7	0.362	32	4.05	0.359
28	4.65	0.354	38	2.85	0.350
		Av. 0.352			Av. 0.347

That the reaction is heterogeneous was clearly shown by a series of preliminary runs in which the rate of decomposition varied slightly and in a reproducible manner from one test tube to another. Therefore, to prevent any further alteration of the active surface in subsequent runs, the reaction tubes were washed with distilled water only between runs and were never allowed to dry. The reactions, the results of which are reported below, were all carried out in the same test tube. In addition, two other similar reactions with hydrogen peroxide in distilled water were carried out simultaneously to provide a check. The course of the reaction was followed analytically. A small portion, about 0.2 cc., of the reaction mixture was quickly removed by means of a pipette, weighed accurately, and titrated against 0.1 N potassium permanganate. This procedure was chosen in preference to the gas evolution method. The solubility of oxygen in the reaction mixture introduces appreciable errors in the latter method unless the liquid is well stirred, a procedure not suitable in the case of a heterogeneous catalysis.

The results are given in Table I, the runs being numbered in the order in which they were carried out. The velocity constant, K, was calculated by means of the equation:

$$K = \frac{1}{t} \frac{2.303}{(OH^-)} \log \frac{a}{a - x},$$

in terms of hours and moles of sodium hydroxide per litre. Since the rates of the reactions investigated here were rather small on account of the analytical method used, and since no critical value is claimed for the present results, it was not considered expedient to express the velocity constant in terms of the customary time units. As may be seen from the plot of these results in Fig. 1, the reaction is first order in both cases. The addition of heavy water to the reaction mixture has reduced the rate of decomposition of the peroxide to about one-quarter of its original value.
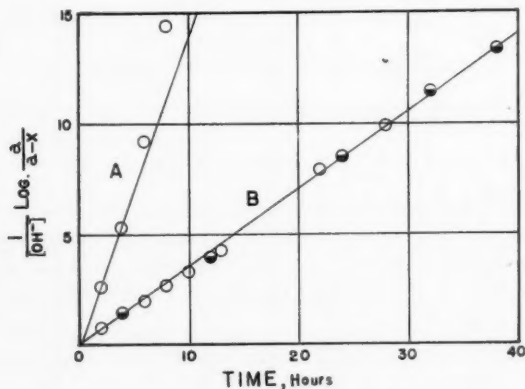

FIG. 1.   *Rate of decomposition on glass of hydrogen peroxide dissolved in ordinary water, Curve A: and in heavy water, Curve B,* ⊙ *Run No. 2:* ⬤ *Run No. 4.*

Catalytic Decomposition on Gold

The decomposition of hydrogen peroxide on the surface of noble metals was first studied by Bredig and Teletow (3). The mechanism of the reaction is rather complex owing to such phenomena as the absorption of hydrogen peroxide on the catalyst and the diffusion of the reactants and products to or from the active surface. A number of metals in various forms were tested in order to secure reasonable and reproducible rates of reaction. The catalyst that gave the best results for the purpose sought here consisted of a piece of gold foil, about 0.5×2 cm., rolled in a spiral. It was first cleaned quickly in aqua regia and washed thoroughly in redistilled water. At the start the catalyst exhibited violent activity, but after a single run this decreased to a reasonable level and became constant. Quite reproducible results could then be obtained if the foil was not allowed to dry between runs. The reactions were carried out in the same way as for the catalysis on glass, the addition of alkali to the reaction mixture being omitted.

TABLE II

RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE ON METALLIC GOLD

Time, hr.	$a - x$, moles of H_2O_2	$\dfrac{x}{t}$	Time, hr.	$a - x$, moles of H_2O_2	$\dfrac{x}{t}$
In ordinary water					
	Run 1			Run 3	
0	12.65	—	0	12.65	—
1	11.5	1.15	2	10.0	1.33
3	8.3	1.45	4¼	5.6	1.66
4	6.35	1.57	5	4.15	1.70
5	4.6	1.61	6	3.0	1.61
7	2.2	1.49			
		Av. 1.46			Av. 1.45
In heavy water					
	Run 2			Run 4	
0	12.35	—	0	12.0	—
4	12.1	0.06	2	11.9	0.05
6	11.8	0.09	6	11.4	0.10
10	11.5	0.085	10½	10.65	0.13
12	11.15	0.10	22	6.75	0.24
18	9.9	0.135	24	5.7	0.26
22	8.6	0.17	26	4.7	0.28
26	6.9	0.21	28	3.6	0.30
28	5.75	0.235	30	2.6	0.315

The catalysis of hydrogen peroxide on gold in ordinary water is a zero order reaction.   Thus the results given in Table II, and plotted in Fig. 2, curve A, follow roughly the equation:
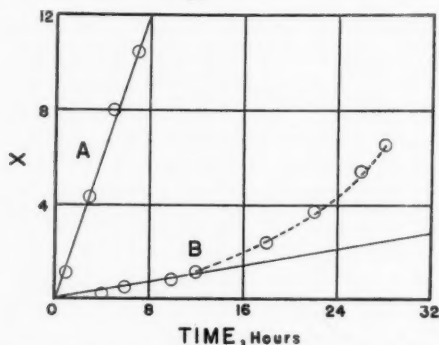
$$\frac{dx}{dt} = K.$$

FIG. 2.   *Rate of the gold catalysis of hydrogen peroxide in ordinary water, Curve A: and in heavy water, Curve B.*

This is not the case, however, when heavy water is added to the peroxide: in Runs 2 and 4 the value of the ratio x/t increases continuously with time. Of a number of differential equations tried, only the following was found to give a roughly constant value of K:

$$\frac{dx}{dt} = Kx.$$

The application of this relationship to Run 2 is illustrated in Fig. 3.   This peculiar result suggests the possibility that some autocatalysis takes place. It must be emphasized, however, that until further experimental results are available, no undue significance should be attached to this observation.
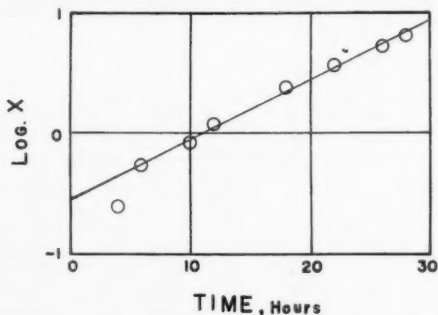

FIG. 3.   *The relationship: Log x vs. t in the case of the catalysis of hydrogen peroxide by gold in heavy water; Run No. 2.*

An explanation of the mechanism of the reactions involved in this case, as well as for the glass catalysis described above, will require more numerous

and diversified data than those presented here, and will also have to take into account the following considerations: When heavy water is added to hydrogen peroxide these exchange reactions take place:

$$H_2O_2 + D_2O = H_2O + D_2O_2 \tag{1}$$
$$H_2O_2 + D_2O_2 = 2HDO_2 \tag{2}$$
$$H_2O + D_2O = 2HDO . \tag{3}$$
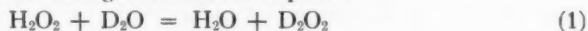
Because of the ionic character of the reacting molecules, these reactions take place readily, as has been shown by the experiments of Erlenmeyer and Gärtner (4). The equilibrium constant for Equation (1) is equal to 1, whereas that of Equation (2) can be assumed to lie close to the value of 3.27 (8) found for Equation (3). The decomposition itself proceeds at various rates according to the three equations:

$$H_2O_2 = H_2O + \tfrac{1}{2}O_2 \tag{4}$$
$$D_2O_2 = D_2O + \tfrac{1}{2}O_2 \tag{5}$$
$$HDO_2 = HDO + \tfrac{1}{2}O_2 \tag{6}$$

so that the three types of water molecules thus formed react again in solution according to Equations (1), (2), or (3).

## Note on Decomposition of Hydrogen Peroxide by Metals

At this point it may be of interest to mention the mechanism proposed recently by Weiss (9) for explaining the catalytic decomposition of hydrogen peroxide by metals. It involves an electron transfer from the metal to the peroxide, which then acts as an oxidizing agent and is split according to the reaction:

$$H_2O_2 + M = M^+ + OH + OH^-$$
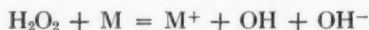
with subsequent chain reactions such as:

and:
$$H_2O_2 + OH = H_2O + HO_2$$
$$O_2^- + H_2O_2 = OH^- + OH + O_2 .$$
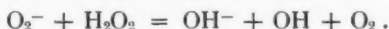
On the other hand, Heyrowsky (5) has shown, by application of the classical theory of overpotential in light and heavy water, that the electro-reduction of hydrogen peroxide in D_2O takes place at a considerably more electronegative potential than the same process in H_2O. Therefore the results presented here are consistent with this mechanism.

The limited quantity of heavy water available at the time the work was done did not permit extension of the scope of this investigation, but the purpose for which it was intended has been fulfilled.

References

1. ABEL, E., REDLICH, O., and STRICKS, W. Naturwissenschaften, 22 : 525. 1934.
2. ABEL, F., REDLICH, O., and STRICKS, W. Monatsh. 65 : 380-385. 1935.
3. BREDIG, G. and TELETOW, J. Z. Elektrochem. 12 : 581–585. 1906.
4. ERLENMEYER, H. and GÄRTNER, H. Helv. Chim. Acta, 17 : 970-973. 1934.
5. HEYROWSKY, J. Coll. Czechoslov. Chem. Commun. 9 : 207-237; 273-301. 1937.
6. OLIVERI-MANDALÀ, E. and INDOVINA, R. Gazz. chim. ital. 67 : 53-55. 1937.
7. RICE, F. O. J. Phys. Chem. 31 : 1352-1356. 1927.
8. TOPLEY, B. and EYRING, H. J. Chem. Phys. 2 : 217-230. 1934.
9. WEISS, J. Trans. Faraday Soc. 31 : 1547-1557. 1935.

DERIVATIVES OF SUBSTITUTED SUCCINIC ACIDS

IV. THE ACTION OF ALKALINE SODIUM HYPOBROMITE ON SOME α-ALKYL-α'-ARYLSUCCINAMIDES[1]

By John A. McRae[2] and Norah A. McGinnis[3]

Abstract

The action of alkaline sodium hypobromite on α-methyl-α'-phenylsuccinamide produces methylphenyldihydrouracil. With the same reagent α-n-hexyl-α'-phenylsuccinamide gives α-n-hexyl-β-ureido-β-phenylpropionic acid. Hence these amides of the α-alkyl-α'-arylsuccinamide type in this reaction resemble the monoalkyl- and monoarylsuccinamides and not the αα'-diarylsuccinamides.

It was shown by McRae, Weston, and Hubbs (6) that phenylsuccinamide and αα'-dimethylsuccinamide behave in the Hofmann reaction in the same manner as do the monoalkylsuccinamides, giving phenyl- and dimethyldihydrouracil respectively. The former amide was taken as probably typical of monoarylsuccinamides and the latter of αα'-dialkylsuccinamides. In order to trace further whether or not the rearrangements to diarylacetic acids of αα'-diarylsuccinamides are confined to substances of that type, three α-alkyl-α'-arylsuccinamides, namely α-methyl-α'-phenyl-, α-n-hexyl-α'-phenyl- and α-benzyl-α'-phenylsuccinamide, have been prepared and their behaviour towards alkaline sodium hypobromite examined.

This examination has shown that the first of these amides gives a disubstituted dihydrouracil, and the second, a ureido-acid, coming doubtless from a dihydrouracil. Paucity of material has left the examination of the third incomplete but it is clear from the behaviour of the first two that substances of this mixed type which, of the several types that have now been studied, are most closely allied to αα'-diarylsuccinamides, do not undergo rearrangement to alkylarylacetic acids.

From the action of sodium hypobromite on α-methyl-α'-phenylsuccinamide, the compound 5-methyl-6-phenyldihydrouracil was isolated. A comparison of the substance isolated with an authentic specimen of this dihydrouracil prepared according to Posner's description (7) showed their virtual identity, although a slight discrepancy in melting points was observed. A mixed melting point determination produced no depression, whereas with the isomeric 5-phenyl-6-methyldihydrouracil, which the substance isolated might have been, a very marked depression of the melting point was observed. Hence it is the amide group attached to the same carbon atom as the phenyl group that is attacked by the hypobromite. The acid isolated from the action of sodium hypobromite on hexylphenylsuccinamide is assumed to be α-n-hexyl-β-ureido-β-phenylpropionic acid $C_6H_5CH(NHCONH_2).CH(C_6H_{13})CO_2H$. The

analytical figures agree with this formula, and it is furthermore assumed that a dihydrouracil has been formed first and that the same amide group as in the previous example has been attacked by the hypobromite.

An attempt was made to prepare in quantity the necessary succinic acids by the method of Zelinski (9), namely, by acting on the sodio-derivative of the appropriate alkylmalonic ester with ethyl α-bromophenylacetate, but the method in the writers' hands did not give sufficiently good yields. We resorted to an application of the method of Lapworth and McRae (4) to prepare methylphenylsuccinic and hexylphenylsuccinic acids. Knowles and Cloke (2) showed that acetaldehyde and phenylacetonitrile can be condensed readily to give α-phenylcrotonic nitrile. By heating this nitrile in alcoholic solution with potassium cyanide, hydrogen cyanide addition takes place and the addition product hydrolyzes in situ to methylphenylsuccinic acid. McRae and Manske (5) described the preparation of α-n-hexylcinnamonitrile and showed that it reacts with potassium cyanide to add on hydrogen cyanide. The addition resulted in a product which was not fully characterized at that time, but it has now been found that the principal substance formed in the addition is the half-nitrile of α-n-hexyl-α'-phenylsuccinic acid. Since diphenyl-succinonitrile hydrolyzes with considerable difficulty it may be concluded that this half-nitrile is α-n-hexyl-β-cyano-β-phenylpropionic acid, $C_6H_5CH(CN)$. $CH(C_6H_{13})CO_2H$. It could be hydrolyzed to hexylphenylsuccinic acid only by heating with concentrated hydrochloric acid in sealed tubes. This is in agreement with the structure assigned, but the ease of hydrolysis of methyl-phenylsuccinonitrile is in marked contrast to the behaviour of hexylphenyl-succinonitrile and also of diphenylsuccinonitrile towards hydrolytic agents. Benzylphenylsuccinic acid was prepared according to Zelinski's method.

It was found that all three of these succinic acids could be converted into their amides more easily by heating the imides with alcoholic ammonia than by acting on the methyl esters with ammonia.

Experimental

α-*Methyl-α'-phenylsuccinic Diamide*, CH_3 . $CH(CONH_2)$. $CH(C_6H_5)CONH_2$

(a) *Methylphenylsuccinic Acid.* α-Phenylcrotonitrile was prepared accord-ing to the directions of Knowles and Cloke (2). A mixture of this nitrile (35.7 gm.) dissolved in 200 cc. of 95% ethyl alcohol with a solution of 32.5 gm. of potassium cyanide in 40 cc. of warm water was refluxed four hours. The mixture was then poured on ice, filtered from a small amount of solid which separated, and extracted thoroughly with ether to remove a small amount of orange-coloured oil. The solution was then acidified with hydrochloric acid and aspirated for 48 hr. Crystals of the desired acid separated in good yield and a further quantity was obtained by evaporating down to small volume. Twenty grams of methylphenylsuccinic acid once recrystallized was obtained from 35.7 gm. α-phenylcrotononitrile. After several recrystallizations from hot water the methylphenylsuccinic acid so obtained melted at 173° to 174° C.*

* *Melting points are corrected.*

Zelinski (9) gives the melting point as 169° to 172°. Equivalent: Found; 108.7. Calc. for $C_{11}H_{12}O_4$; 109.

(*b*) *α-Methyl-α'-phenylsuccinimide*. This imide was prepared by converting methylphenylsuccinic acid into its ammonium salt and heating the dry salt in a Claisen flask for four hours at 180°. The residue was then distilled under reduced pressure; it passed over at 219° to 225° C. at 8 mm., condensing as a greenish viscous liquid which solidified slowly. After rubbing up with ether the residual solid was recrystallized repeatedly from alcohol, whereupon it was obtained as hard needles. M.p. 109° C. Calc. for $C_{11}H_{11}O_2N$: N, 7.42%. Found: N, 7.22%.

(*c*) *α-Methyl-α'-phenylsuccinamide*. The imide was converted into the amide by heating with alcoholic ammonia for four days at 80° to 100° C. The yield was 75% of the calculated. The substance produced on repeated recrystallization from ethyl alcohol melted at 224° to 225° C. Calc. for $C_{11}H_{14}O_2N_2$: N, 13.59%. Found: N, 13.62%.

(*d*) *Action of Sodium Hypobromite on Methylphenylsuccinamide*. Methylphenylsuccinamide (6.9 gm.), made into a thin paste with water, was added slowly with efficient stirring to a solution made from 10.7 gm. of bromine added to 13.4 gm. of caustic soda in 70 cc. of water at −10° C. The temperature was maintained below −5° during the addition of the amide, and after the mixture had stood in the cold for 30 min. it was allowed to come to room temperature, and 8.0 gm. of caustic soda was added. Stirring was continued for an additional 30 min. and then the mixture was heated for three hours at 70° to 80°. During the heating a little ammonia was evolved. The solution was cooled, diluted, and acidified. Ether extracted a very small amount of oil (possibly the ureido-acid corresponding to the dihydrouracil). By evaporating down the aqueous portion, 3.0 gm. of crystalline substance was obtained which, recrystallized repeatedly from hot water, had a melting point of 192° to 195° C. This substance seems to be 5-methyl-6-phenyl-dihydrouracil

$$C_6H_5 . CH . NH . CO$$
$$CH_3 . CH—CO—NH$$
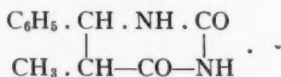
Calc. for $C_{11}H_{12}O_2N_2$: N, 13.74%. Found: N, 14.01%.

For comparison a sample of this dihydrouracil was prepared according to Posner's directions (7) after it was found that the general method of Fischer and Roeder (1) gave little or none of the desired substance. Posner gave m.p. 185° C. (uncorr.) and our specimen prepared according to his directions melted at 188° to 191°. This substance and that made from methylphenylsuccinamide on admixture melted at 191° to 193°. There is a slight difference in the appearance of the two substances. Posner's methylphenyldihydrouracil was obtained in the form of granular acicular crystals, whereas the crystals of the substance isolated from methylphenylsuccinamide felted together. A comparison of these two substances under the polarizing microscope was kindly made for us by Prof. J. E. Hawley. It showed that the

substance made from the succinamide occurs in rectangular plates belonging to the orthorhombic system and shows parallel extinction. The indices of refraction are N_p or $N_\alpha = 1.570$, N_g or $N_\gamma = 1.665$ and N_m or $N_\beta < 1.665$ and > 1.629. Posner's methylphenyldihydrouracil was obtained in much finer grains and was of a more acicular habit. This substance likewise shows parallel extinction and has the following indices of refraction: N_α, 1.570; N_β, 1.665 and $N_\gamma < 1.665$. The conclusion from this examination was that the difference between the two appears to be only that of grain size. It may be however that the differences actually observed are due to the fact that the two substances are not identical but rather geometrical isomerides.

5-Phenyl-6-methyldihydrouracil.

$$CH_3 . CH . NH . CO$$
$$C_6H_5 . NH . CO . NH$$
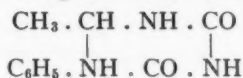
This substance was prepared also for purposes of comparison. The general method of Posner was applied. Difficulty was experienced in getting good yields of α-phenylcrotonic acid according to the directions of Rupe and Busolt (8) from paraldehyde and sodium phenylacetate. The acid was esterified with methyl alcohol and the methyl ester heated with a solution of hydroxylamine. The amino-acid thus formed was treated with potassium cyanate. The ureido-acid formed from this acid was not characterized but converted into the dihydrouracil.

α-Phenyl-β-aminobutyric Acid

Methyl α-phenylcrotonate (29.5 gm.) was refluxed for three and one-half hours with 7.0 cc. of 1-molar hydroxylamine solution in methyl alcohol prepared according to Posner. On standing overnight the amino-acid separated in crystalline form. Yield, 19 gm. For analysis the substance was recrystallized repeatedly from hot water. M.p. 248° C. Calc. for $C_{10}H_{13}O_2N$: C, 67.04; H, 7.31; N, 7.87%. Found: C, 67.3; H, 7.36; N, 7.30%.

α-Phenyl-β-ureidobutyric Acid and 5-Phenyl-6-methyldihydrouracil

Nineteen grams of the foregoing amino-acid was suspended in 500 cc. of water, heated on the water bath and stirred while 19 gm. of potassium cyanate was added. The stirring was continued for one hour and then the mixture was strongly acidified; this caused the separation of a precipitate, partially gummy and partially crystalline. No attempt was made to isolate the ureido-acid in a pure condition from this material, but it was heated to 125° until effervescence ceased. The residue, which was the desired dihydrouracil, was recrystallized from ethyl alcohol, in which it is difficultly soluble. It separated in glistening elongated hexagonal plates, m.p. 224° C. Calc. for $C_{11}H_{12}O_2N$: C, 64.71; H, 5.88; N, 13.73%. Found: C, 65.05; H, 6.11; N, 13.75%. This dihydrouracil, mixed with the Posner product, melted indefinitely from 172° to 178°, and, with that from methylphenylsuccinamide, from 172° to 188°.

α-n-Hexyl-α'-phenylsuccinic Diamide $C_6H_5CH(CONH_2) . CH(C_6H_{13}) . CONH_2$

(a) *α-n-Hexyl-β-cyano-β-phenylpropionic Acid* $C_6H_5(CN) . CH . CH(C_6H_{13})$ CO_2H. This acid was made from the addition product of hydrogen cyanide

to heptylidene-benzyl cyanide (5). Heptylidene-benzyl cyanide (23 gm.) was dissolved in ethyl alcohol (150 cc.) and mixed with 13 gm. of potassium cyanide in 25 cc. of water. The mixture was refluxed for four hours on the water bath, whereupon a clear reddish solution was obtained. Longer heating is to be avoided. On pouring into water a slight precipitate formed. After removing it the solution was acidified; this precipitated 19.5 gm. of the above-mentioned acid. For purification the substance was recrystallized from hot dilute alcohol. M.p. 166°. Calc. for $C_{16}H_{21}O_2N$: C, 74.13; H, 8.11; N, 5.41%. Found: C, 74.02; H, 8.19; N, 5.31%. $C_{16}H_{21}O_2N$ requires an equivalent of 259. Equivalent found: 259.

(b) α-n-Hexyl-α'-phenylsuccinic Acid. The foregoing acid, the half-nitrile of hexylphenylsuccinic acid, proved difficult to hydrolyze. The usual alkaline and acidic hydrolyzing agents either left the material unattacked or else produced gums which resisted purification. The method which proved most satisfactory was to heat the nitrile-acid with four times its weight of concentrated hydrochloric acid in a sealed tube for 12 hr. at 150° to 170°. Even then the acid was not obtained in a form sufficiently pure for characterization, but it was converted into the imide.

(c) α-n-Hexyl-α'-phenylsuccinimide. This imide was prepared from the acid in the same manner as methylphenylsuccinimide. On distillation after heating the ammonium salt of the succinic acid it passed over at 211° to 215° at 1 mm. The viscous distillate dissolved on being rubbed with dilute ammonia and the crystalline imide separated on standing. This material easily became oily again but by triturating several times with petroleum ether it was obtained in a colourless crystalline form apparently analytically pure. M.p. 52°. Calc. for $C_6H_2O_3N$: C, 74.1; H, 8.11; N, 5.48%. Found: C, 73.8; H, 8.19; N, 5.38%.

(d) α-n-Hexyl-α'-phenylsuccinamide. This substance was obtained by heating the imide in a sealed tube with alcoholic ammonia for 48 hr. at 80° to 100°. Ten grams of crude amide was obtained from 18.0 gm. of imide. The product was recrystallized from alcohol. M.p. 233°, with decomposition. Calc. for $C_{16}H_{24}O_2N_2$: N, 10.14%. Found: N, 10.13%.

(e) Action of Sodium Hypobromite on Hexylphenylsuccinamide. Hexylphenylsuccinamide (8.9 gm.), made into a thin paste with water, was mixed at 5° with an alkaline solution of sodium hypobromite made from 12.8 gm. of sodium hydroxide in 70 cc. of water by the addition of 10.3 gm. of bromine at −10°. The mixture was treated as described for methylphenylsuccinamide. During the heating on the water bath, ammonia was given off. A small amount of oil separated on cooling. After extraction of this oil the residual solution was acidified when 5.8 gm. of a yellow gum separated. The gum, after drying, was triturated with dry ether. This left a product which, after several recrystallizations from dilute alcohol, melted at 144° to 145° with decomposition. This substance is evidently α-n-hexyl-β-phenylureidopropionic acid $C_6H_5CH(NHCONH_2) . CH . (C_6H_{13})CO_2H$. Calc. for $C_{16}H_{24}O_3N$:

N, 9.59%.   Found: N, 9.63%. $C_{16}H_{24}O_3N$ requires equivalent: 292. Found equivalent: 292.9.

α-Benzyl-α'-phenylsuccinic Diamide

(a) *α-Benzyl-α'-phenylsuccinimide.*   Benzylphenylsuccinic acid was made from benzylmalonic ester and α-bromophenylacetic ester according to the directions of Kögl and Becker (3). From it the imide was prepared as described for methylphenylsuccinimide. The distillate obtained solidified and the material was recrystallized from alcohol. M.p. 131°. Calc. for $C_{17}H_{15}ON$: N, 5.28%. Found: N, 5.62%.

(b) *α-Benzyl-α'-phenylsuccinamide.*   This amide proved difficult to obtain. The imide of this succinic acid was heated with alcoholic ammonia in a sealed tube for three weeks at 80° to 100°. The yield of crude amide from 13.1 gm. of imide was 8.8 gm. The substance was purified by recrystallization from alcohol. M.p. 216°. Calc. for $C_{17}H_{18}O_2N_2$: N, 9.93%. Found: N, 10.00%.

(c) *Action of Sodium Hypobromite on Benzylphenylsuccinamide.*   Benzyl-phenylsuccinamide was treated with alkaline sodium hypobromite first in the cold and then at 80° as described for the other two amides. A small amount of alkali-insoluble material remained after the alkaline treatment. Acidification of the filtrate produced a gum which became solid on standing. Repeated recrystallizations gave ultimately a substance of m.p. 219°. Analyses of this product by two microanalysts gave inconsistent results. Neither figures agreed with those calculated from the formulae of possible substances. Lack of material has prevented further examination of the material but it is our intention to re-examine the products of this reaction later.

Acknowledgments

References

1. FISCHER, E. and ROEDER, G. Ber. 34 : 3751-3763. 1901.
2. KNOWLES, E. C. and CLOKE, J. B. J. Am. Chem. Soc. 54 : 2028-2037. 1932.
3. KÖGL. F. and BECKER, H. Ann. 465 : 211-242. 1928.
4. LAPWORTH, A. and McRAE, J. A. J. Chem. Soc. 121 : 1699-1712. 1922.
5. McRAE, J. A. and MANSKE, R. H. J. Chem. Soc. : 484-491. 1928.
6. McRAE, J. A., WESTON, A. W., and HUBBS, C. F. Can. J. Research, B, 15 : 434-437. 1937.
7. POSNER, T. Ann. 389 : 1-120. 1912.
8. RUPE, H. and BUSOLT, E. Ann. 369 : 318-339. 1909.
9. ZELINSKI, N. Ber. 21 : 3160-3172. 1888.
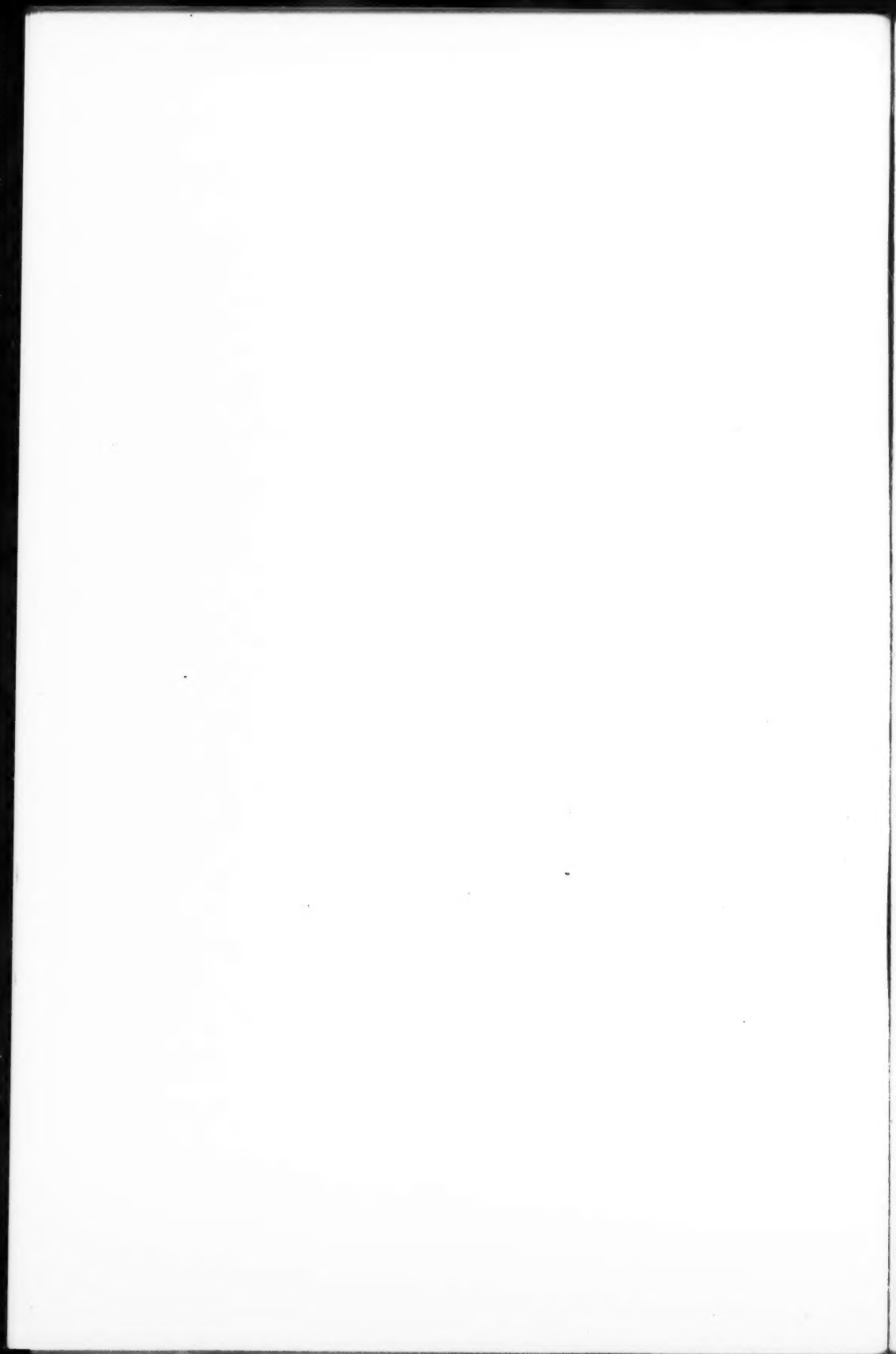
CANADIAN JOURNAL OF RESEARCH

Notes on the Preparation of Copy

General:—Manuscripts should be typewritten, double spaced, and the original and one copy submitted. Style, arrangement, spelling, and abbreviations should conform to the usage of this Journal. Names of all simple compounds, rather than their formulae, should be used in the text. Greek letters or unusual signs should be written plainly or explained by marginal notes. Superscripts and subscripts must be legible and carefully placed. Manuscripts should be carefully checked before being submitted, to reduce the need for changes after the type has been set. All pages should be numbered.

Abstract:—An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required.

Illustrations:—Drawings should be carefully made with India ink on white drawing paper, blue tracing linen, or co-ordinate paper ruled in blue only. Paper ruled in green, yellow, or red should not be used. The principal co-ordinate lines should be ruled in India ink and all lines should be of sufficient thickness to reproduce well. Lettering and numerals should be of such size that they will not be less than one millimetre in height when reproduced in a cut three inches wide. If means for neat lettering are not available, lettering should be indicated in pencil only. All experimental points should be carefully drawn with instruments.

Illustrations need not be more than two or three times the size of the desired reproduction, but the ratio of height to width should conform with that of the type page. Small photographs should be mounted on cardboard and those to be reproduced in groups should be so arranged and mounted. The author's name, title of paper, and figure number should be written on the back of each illustration. Captions should not be written on the illustrations, but typed on a separate page of the manuscript.

Tables:—Titles should be given for all tables, which should be numbered in Roman numerals. Column heads should be brief and textual matter in tables confined to a minimum.

References should be listed alphabetically by authors' names, numbered in that order, and placed at the end of the paper. The form of literature citation should be that used in this Journal and titles of papers should not be given. All citations should be checked with the original articles.

The *Canadian Journal of Research* conforms in general with the practice outlined in the *Canadian Government Editorial Style Manual*, published by the Department of Public Printing and Stationery, Ottawa.